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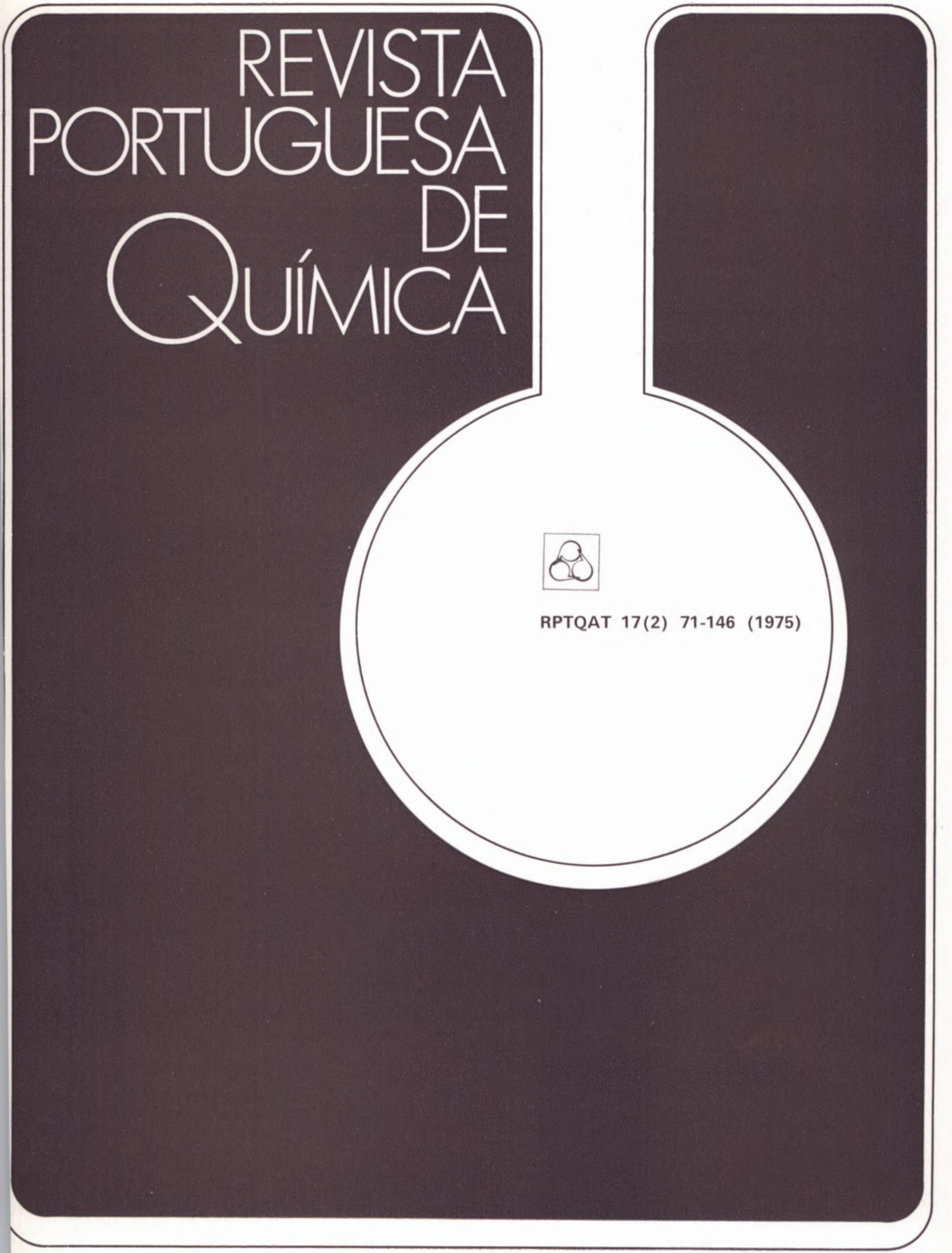

RPTQAT 17(2) 71-146 (1975)

índice

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MULTICOMPONENT DISTILLATION EFFICIENCY STUDIES IN A LOW SEPARATION COLUMN (2)

In the design of distillation equipment the estimation of plate efficiency is still a major problem. For multicomponent systems the problem is aggravated by the possibility of different values for the efficiency of each component present.

A further difficulty is the choice of a suitable definition of efficiency and it is suggested that a comparison between different efficiency definitions is more meaningful if results are used from low efficiency apparatus.

In this work the ternary system Benzene/Methylcyclohexane/ /Toluene is studied in a two inches diameter, eight plate, Pool column and the results are interpreted as both «Murphree type» efficiencies and vaporization efficiencies.

With the overall separation achieved in the Pool column, the results are particularly susceptible to experimental errors in measured compositions. However it is shown that Murphree efficiencies are relatively constant with little variation between different components. Interpreting the results as vaporization efficiencies gives values varying between 60 % and 200 %; limitations of this type of definition are discussed based on these values.

1 — INTRODUCTION

Since in a distillation operation equilibrium between liquid and vapour streams leaving a plate is not generally reached, efficiencies have to be considered.

LEWIS (1922) introduced the simple concept of overall efficiency.

$$E_{OV} = \frac{N_I}{N_R} \tag{1}$$

where

N_I — number of theoretical plates
N_R — number of real plates

The simplicity of this definition is overshadowed by the difficulties involved in its prediction. Also the fact that it is based on the assumption of equal reflux ratios and product compositions implies that equal efficiencies must exist for the different components.

MURPHREE (1925) introduced a definition of plate efficiency which compares the separation achieved by an actual plate with that of a theoretical plate. Refering to fig. 1 MURPHREE vapour phase efficiency for plate n and component i may be written as:

$$E_{MVn,i} = \frac{y_{n,i} - y_{n+1,i}}{(y^*_{n,i})_M - y_{n+1,i}} \tag{2}$$

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This paper was presented at the Transport processes section, where

$y_{n,i}$ and $y_{n+1,i}$ — are the mole fractions of component i in the vapour leaving and entering plate n respectively.

$(y^*_{n,i})_M$ — mole fraction of component i in the vapour in equilibrium with the liquid leaving plate n considered as a saturated liquid.

Similarly Murphree's liquid phase efficiency for component i and plate n can be written as:

$$E_{MLn,i} = \frac{x_{n-1,i} - x_{n,i}}{x_{n-1,i} - (x^*_{n,i})_M} \tag{3}$$

where

$x_{n-1,i}$ and $x_{n,i}$ — mole fractions of component i in the liquid entering and leaving plate n respectively.

$(x^*_{n,i})_M$ — mole fraction of component i in the liquid in equilibrium with the vapour leaving plate n, considered as a saturated vapour.

Limitations of the Murphree definition were discussed by STANDART (1965) and may be summarized as follows:

(i) It is unsatisfactory for a single actual plate to have two unequal efficiencies for each component; generally $E_{MVn,i} \neq E_{MLn,i}$

(ii) There is a mass balance discrepancy between the two definitions.

(iii) There is no reason to assume that either phase needs to be saturated.

A more satisfactory Murphree type efficiency was defined by HAUSEN (1953)

$$E_{Hn,i} = \frac{y_{n,i} - y_{n+1,i}}{(y^*_{n,i})_H - y_{n+1,i}} \tag{4}$$

where

$(y^*_{n,i})_H$ — mole fraction of component i in the vapour which results from a flash calculation with a feed composition equal to the sum of the streams entering the plate.

A different concept of plate efficiency, the vaporization efficiency, was introduced by TAYLOR (1962) and HOLLAND (1963)

$$E_{vn,i} = \frac{y_{n,i}}{Y_{n,i}} \tag{5}$$

where

$Y_{n,i} = K_{n,i}x_{n,i}$ and $K_{n,i}$ — vapour liquid equilibrium ratio evaluated at the actual temperature and pressure at which the liquid leaves plate n.

The relative merits of the different approaches to the definition of plate efficiency have been discussed by GUCALP (1966), HOLLAND and MCMAHON (1970), STANDART (1971), MISKIN, OZALP and ELLIS (1972) and ASHTON, MEDINA and MCDERMOTT (1975).

In the present paper experimental results obtained for the system Benzene/Methylcyclohexane (M.C.H.)/Toluene on a column of inherently low efficiency are presented and are treated both as Murphree and vaporization efficiencies; the low separation of the column exagerates the differences between the two models.

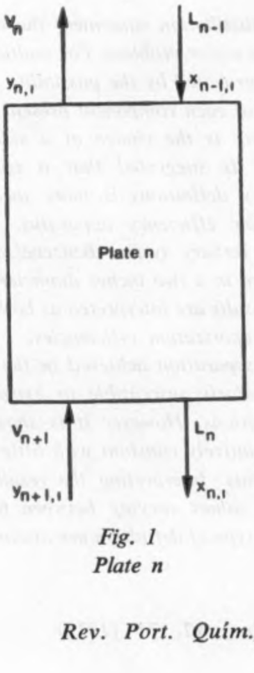

Fig. 1
Plate n

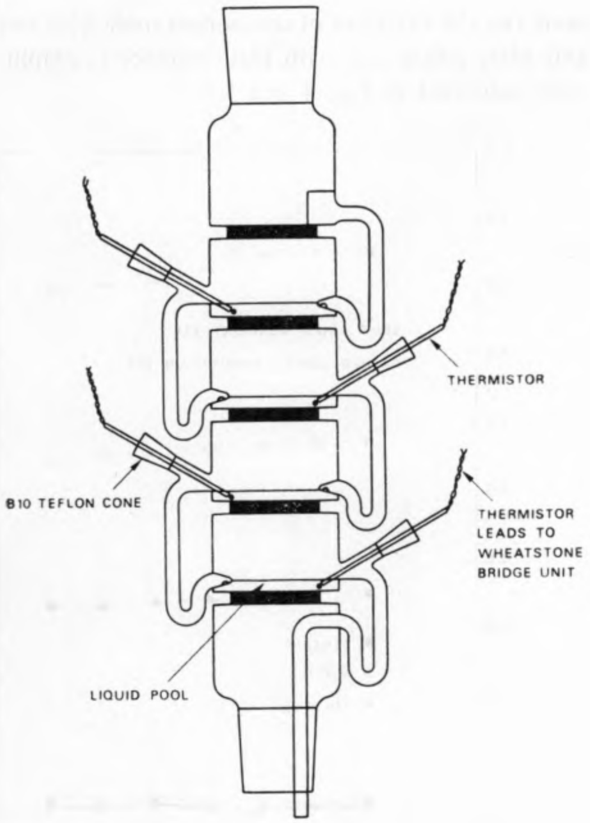

Fig. 2
Four plate Pool column

2 — EXPERIMENTAL APPARATUS

The Pool column was first introduced by BIDDULPH (1966) and further developed by HARDWICK (1971). The original concept was to have a contacting device of known and constant interfacial area. Hence, the vapour flows across the surface of the liquid.

A four plate column is shown in fig. 2 and the overall arrangement of the apparatus is presented in fig. 3. Vapour leaving reboiler A, flows through the side arm of bottom ratemeter B into the column. The column consists of eight plates, 5 cm diameter. Leaving the column through vapour riser D, the vapour passes through a short section of Knitmesh packing before being totally condensed in condenser F. The liquid reflux is raised to saturation temperature by contact with the ascending vapour in the packed section E and flows to the top plate via a ratemeter G.

Liquid samples could be removed simultaneously from all eight plates using an array of hypodermic syringes. These were mounted in a ice-cooled box and were connected to the column using 0.8 mm capillary stainless steel tubes.

Plate temperatures were measured using thermistors coupled to a Wheatstone bridge circuit enabling an accuracy of ± 0.05 °C to be achieved over the range 50-150 °C.

The column was enclosed in a heated asbestos box to maintain adiabatic operating conditions.

3 — EXPERIMENTAL SYSTEM

The system used was Benzene/Methylcyclohexane//Toluene which was analysed using a Pye104 Chromatograph with dual flame ionization detector. Analar grades of components were selected and chromatographic tests showed their purity to be better than 99.5 %.

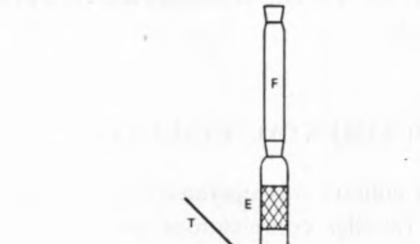

Fig. 3
Experimental apparatus : A — reboiler ; B — bottom ratemeter ; C — column ; D — superheater ; E — knitmesh packing ; F — condenser ; G — top ratemeter ; S — sampling device ; H — heater

Ternary vapour-liquid equilibrium data were predicted using Margules equations; binary parameters were obtained from published binary equilibrium data by direct fitting of Margules equations using the total pressure method of McDermott (1964). Table 1 summarizes the sources of experimental data and calculated Margules constants.

Pure component vapour pressures were evaluated using Antoine equations in the form

$$\log_{10} P_i^s = A_i - \frac{B_i}{C_i + T} \tag{6}$$

where

P_i^s — vapour pressure of component i (mmHg)
A_i, B_i, C_i — Antoine constants of component i
T — temperature (°C)

Values of the Antoine constants used are presented in Table 2.

4 — EXPERIMENTAL RESULTS

The Pool column was operated at total reflux using different reboiler compositions and maintaining a constant F-factor of

$$F = 0.09 \text{ lb}^{1/2} \text{ ft}^{-1/2} \text{ sec}^{-1}$$

Experimental results for a typical run are presented in Table 3 together with calculated values of Murphree and vaporization efficiencies. For the same run the variation of component mole fractions and plate efficiencies with plate number is graphically presented in Fig. 4 and 5.

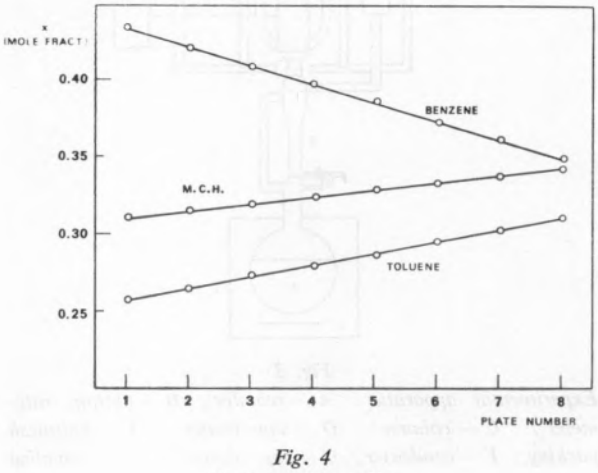

Fig. 4
Composition profiles

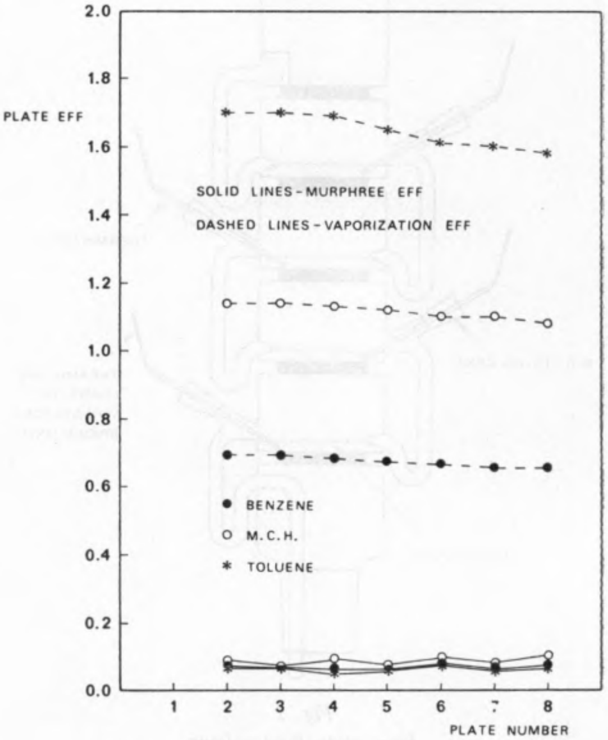

Fig. 5
Variation of plate efficiency with plate number

5 — DISCUSSION OF RESULTS

5.1 — *VAPORIZATION EFFICIENCIES*

It is immediately apparent that the value of the vaporization efficiency is significantly different for the different components. In fact, from the definition of vaporization efficiency this is bound to be the case. As the mole fraction of the more volatile component (MVC) is increasing up the column it can be written that:

$$y_{n,\,MVC} < Y_{n,\,MVC}$$

hence

$$E_{v,\,MVC} < 1$$

Also

$$\lim_{x_{MVC} \to 1} (E_{v,\,MVC}) = 1 \tag{7}$$

Table 1

Vapour-liquid equilibrium data

System	Reference	Margules constants	
		M(1,2)	M(2,1)
Benzene (1)/M.C.H. (2)	Myers (1956)	0.210	0.3848
Benzene (1)/Toluene (2)	Heertjes (1960)	— 0.0304	0.0028
M.C.H. (1)/Toluene (2)	Contractor (1958)	0.2449	0.2106

The mole fraction of the heavy component (less volatile component — LVC) decreases up the column and so

$$y_{n,\ LVC} > Y_{n,\ LVC}$$

and

$$\lim_{x_{LVC} \to 1} E_{v,\ LVC} = 1 \qquad (8)$$

The vaporization efficiencies of the intermediate component may take values either side of the unity depending on the shape of the composition profile.

In fig. 6 component vaporization efficiencies for each run are plotted against average mole fractions. The extreme values of vaporizations efficiencies obtained are as follows:

Component	Vaporization efficiencies	
	Minimum	Maximum
Benzene	0.584	0.840
Methylcyclohexane	0.907	1.245
Toluene	1.350	2.092

In fig. 6 the curves drawn for Benzene and Toluene clearly show the trends previously refered to:

$$\lim_{x_{Benzene} \to 1} E_{v,\ Benzene} = 1$$

$$\lim_{x_{Toluene} \to 1} E_{v,\ Toluene} = 1$$

5.2 — *MURPHREE EFFICIENCIES*

Calculated values of Murphree efficiencies are normally small numbers between 5 % and 10 %,

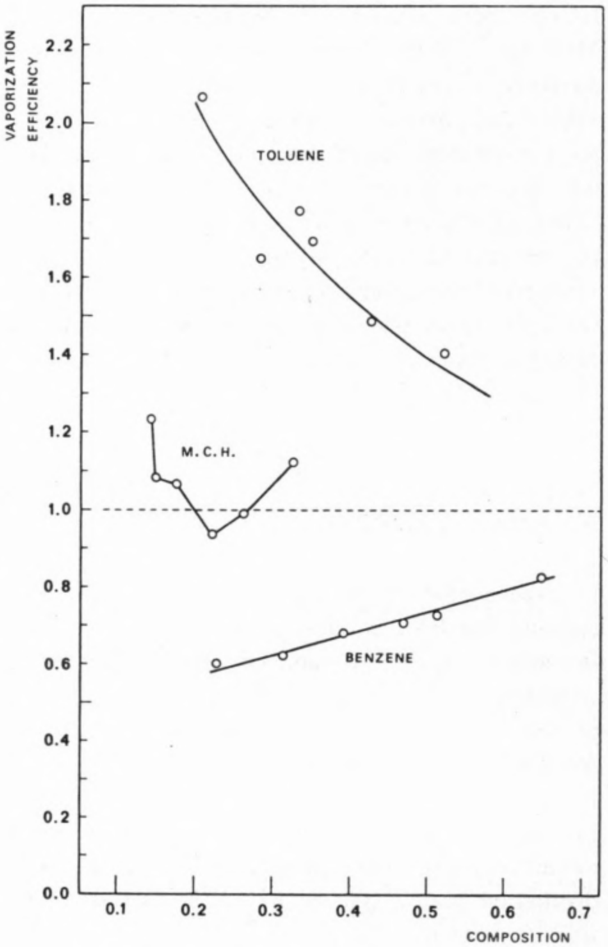

Fig. 6
Variation of vaporization efficiency with composition

Table 2

*Antoine constants (*Boublik et al., *1973)*

Component	A	B	C
Benzene	6.9056	1211.033	220.79
Methylcyclohexane	6.8269	1272.864	221.63
Toluene	6.9533	1343.943	219.38

thus representing well the separation of the Pool column.

So far as the intermediate component is concerned large differences between calculated efficiencies can arise. This, however, can be explained in terms of experimental errors as these are, in some cases, of the order of magnitude of the separation per plate. It has been shown by Ashton, Medina and McDermott (1975) that this doesn't affect the accuracy of any plate to plate calculations in which these values may be involved.

Also if the influence of experimental errors is taken into account it can be shown that the numerical values of Murphree efficiencies of individual components do not differ significantly. They are also similar to the numerical values obtained by Hardwick (1971) for the distillation of the binary system Methylcyclohexane/Toluene.

6 — CONCLUSIONS

1) Experimental work done on a low separation column, the Pool column, with the ternary system Benzene/Methylcyclohexane/Toluene allowed a comparison between two different plate efficiency models to be made in conditions in which their differences were emphasized.

2) The inadequacy of the vaporization efficiency model to describe the behaviour of the phases in distillation plates, due to its mathematical limitations is shown.

Different efficiency values for each component were obtained as the vaporization efficiencies of Benzene are always smaller than unity, those of M.C.H. are close to unity and those of Toluene are always greater than unity reaching values of 200 %.

Table 3

Experimental results on the Pool column

Plate No.	Component	x	E_{MV}	E_v
1	Benzene	0.433		
	M.C.H.	0.310		
	Toluene	0.257		
2	Benzene	0.420	0.073	0.694
	M.C.H.	0.315	0.090	1.14
	Toluene	0.265	0.066	1.70
3	Benzene	0,408	0.068	0.691
	M.C.H.	0,319	0.074	1.14
	Toluene	0.273	0.065	1.70
4	Benzene	0.397	0.062	0.681
	M.C.H.	0.324	0.094	1.13
	Toluene	0.279	0.048	1.69
5	Benzene	0.386	0.062	0.672
	M.C.H.	0.328	0.077	1.12
	Toluene	0.286	0.056	1.65
6	Benzene	0.372	0.078	0.666
	M.C.H.	0.333	0.099	1.10
	Toluene	0.295	0.071	1.61
7	Benzene	0.361	0.062	0.655
	M.C.H.	0.337	0.082	1.10
	Toluene	0.302	0.055	1.60
8	Benzene	0.348	0.073	0.653
	M.C.H.	0.342	0.105	1.08
	Toluene	0.310	0.062	1.58

3) Numerical values of Murphree efficiencies are normally small numbers which are in agreement with physical reality. The influence that experimental errors have on calculated Murphree efficiencies can be large for a small separation column, above all for the intermediate component. However previous work by the same authors (ASHTON *et al.*, 1975) has shown that this doesn't affect plate calculations in which these values may be used.

ACKNOWLEDGEMENTS

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NOTATION

A,B,C	— Antoine constants
E_H	— Hausen plate efficiency
E_{ML}	— Murphree liquid phase plate efficiency
E_{MV}	— Murphree vapour phase plate efficiency
E_{OV}	— overall efficiency
E_v	— vaporization efficiency
F	— F-factor
K	— vapour-liquid equilibrium ratio
M	— Margules constant
N	— number of plates
P^s	— vapour pressure
T	— temperature
x	— liquid mole fraction
y	— vapour mole fraction

SUBSCRIPTS

i	— component i
n	— plate n

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RESUMO

No projecto de colunas de destilação a estimativa de eficiências de prato é um problema fundamental. Em sistemas multicomponentes surgem dificuldades suplementares pela possibilidade de os diferentes componentes terem eficiências diferentes. A escolha do modelo de eficiência mais adequado é um problema ainda em aberto, sugerindo-se que as diferenças entre os diferentes modelos são realçadas se forem utilizados resultados obtidos em colunas de baixa eficiência. No presente trabalho utiliza-se o sistema ternário benzeno/metilcicloexano/ /tolueno em ensaios de destilação realizados numa coluna tipo Pool, de oito pratos, com cinco centímetros de diâmetro, sendo os resultados obtidos interpretados em termos de eficiências de Murphree e de vaporização. Atendendo à pequena separação obtida numa coluna tipo Pool, os resultados são particularmente influenciados por erros experimentais. É possível concluir, no entanto, que a variação de eficiências de Murphree com a composição é pouco significativa. Valores calculados de eficiências de vaporização variam entre 60 % e 200 %; discutem-se limitações deste tipo de eficiências.

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THERMAL CONDUCTIVITY MEASUREMENTS OF N-HEPTANE ALONG THE SATURATION LINE BY A TRANSIENT HOT WIRE TECHNIQUE

The thermal conductivity of liquid n-heptane has been measured at temperatures around room temperature using a transient hot wire technique. The apparatus has been designed so as to minimize all possible spurious effects. The thermal conductivity of the liquid is obtained from the slope of the temperature increase of a 10 μ diameter platinum wire versus logarithm of time. Convection has been avoided by a careful choice of the duration of the experiment; small corrections due to the finite heat capacity of the platinum wire, the bounded medium, the temperature dependence of fluid properties, the finite diameter of the wire, were made. The end effects of the wire have been reduced to less than 0.01 % by a compensation device, employing a shorter wire as another arm of the Wheatstone bridge used for the measurement. An automatic bridge provides the times at which the resistance of the wire reaches six-predetermined values, using a comparator and a crystal controlled clock of 100 kHz with a resolution of ± 10 μsec and working in conjunction with a six-channel counter. The other two arms of the bridge consist of ultrastable metal-film resistors to avoid resistance drifts.

1 — INTRODUCTION

Accurate values of transport properties of liquids are required in order to obtain meaningful information on the intermolecular potential in the repulsive region [1]. The energy transfer between molecules during collision is strongly dependent on the directional forces between molecules and their internal degrees of freedom, and there is still a lot of work to be done on the effect of liquid structure on the transport properties, even for simple molecules (including the light hydrocarbons) before that transfer process is completely understood.

Unfortunately, the data available for the thermal conductivity of liquid hydrocarbons are scarce, and, moreover, there is considerable disparity between the results obtained by different workers and by different techniques. For instance, the available data for the thermal conductivity of satured hydrocarbons at 30 °C, taken from 23 different sources [2] are plotted in fig. 1, showing a considerable scattering of the experimental points, although most of them seem to lie within a band whose width extend from about $\pm 6\%$ for nC_5 to $\pm 2\%$ for nC_{18}. It is thus clear that there is a need for reliable measurements of the thermal conductivity of liquids both for fundamental studies and also for the purposes of optimal technological design.

HAARMAN [3, 4] has now developed a refined theory for the transient temperature behaviour of a thin

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conducting wire, immersed in a fluid, as a result of a step change in the electrical energy dissipated within it. We have thus applied Haarman's theory to the design of an apparatus for the measurement of thermal conductivity of liquids [5], and some preliminary measurements of the thermal conductivity of n-heptane are reported here.

De Groot *et al.* [6] applied recently Haarman's theory to the design of an apparatus to measure the thermal conductivity of gases, and Healy *et al.* [7] developed a complete and up-to-date theory for the transient hot wire which can, in part, be applied to our calculations.

2 — THE APPARATUS

2.1 — *MECHANICAL ASSEMBLY AND THERMOSTATS*

An apparatus for the measurement of thermal conductivity of liquids using a transient hot wire method has been designed and built according to theory and features described elsewhere [5].

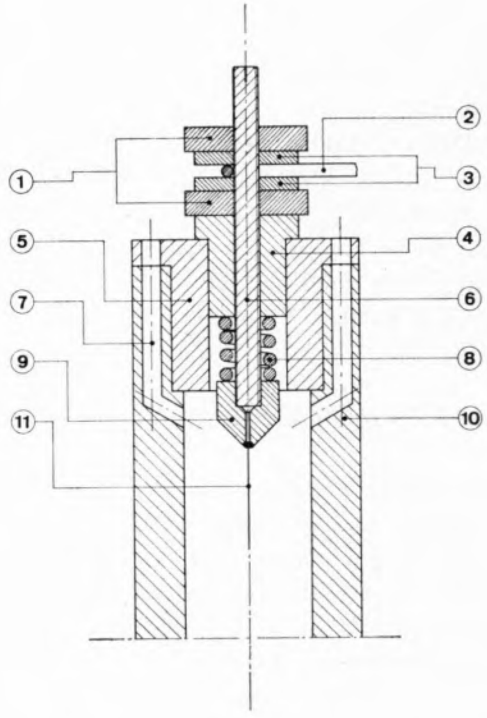

Fig. 2

Adjustment mechanism of the wire
1 — Nut; 2 — electric cable; 3 — metalic ring; 4 — teflon insulation; 5, 10 — cell parts; 6 — adjustment screw; 7 — fluid inlet; 8 — spring; 9 — connection with the Wood metal drop; 11 — platinum wire

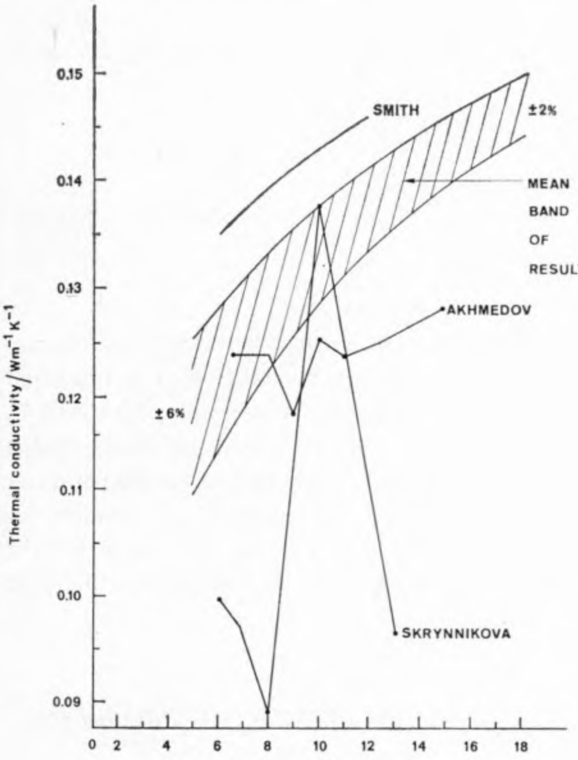

Fig. 1

Diagramatic plot of the thermal conductivity of satured hidrocarbons at 30° C as a function of the number of carbon atoms

Two stainless steel cells, the measuring cell and the compensating one, are immersed in a pressure vessel within a temperature controlled bath. The 10 μ platinum wire used (Goodfellow Metals Ltd.) is connected to the cell ends by means of an adjustment mechanism shown in fig. 2. Because of the delicacy of thin platinum wire, extreme care must be taken while assembling the fluid cell. Good electrical contact with the adjustment mechanism is achieved with a drop of Wood's metal (b.p. ~ 70 °C) near the spot where the platinum wire reaches part 11 on fig. 2. After assembling, the wire is annealed until it becomes incandescent in a dark room for several seconds. Subsequently the wire is stretched with the aid of the screws 6, placed horizontally, and his length measured with a cathetometer within ± 0.01 mm.

The pressure vessel is a standard stainless steel cylinder, fitted with two clamps to hold the cells.

The entire assembly was degreased with Decon 90 solution and acetone.

The pressure vessel was immersed within a temperature controlled bath, consisting of a thermostat (LAUDA, type D40) controlled by a PTR temperature controller (LAUDA type R52 Electronic), and cryostat (HAAKE, type FK2) acting as the cold source. Tests have shown that the temperature stability is very good (around: ± 0.004 K at 288 K and ± 0.01 K at 313 K).

2.2 — *THE ELECTRONICS*

Our measurement technique is similar to that used by HAARMAN [3] and DE GROOT *et al.* [6] in their work for the gas phase. In an earlier communication [5] we have described the principle of the method and the design of the bridge. A high precision Wheatstone bridge with automatic timing and control equipment was built according to the specifications required by the proper design. The details of bridge operation are described elsewhere [17].

3 — EXPERIMENTAL

3.1 — *PURIFICATION OF n-HEPTANE*

Comercial BDH n-heptane, with a purity of no less than 99,5 % was treated with 4A molecular sieves to remove water, degassed in vacuum and then destilled under its own vapour pressure. Its refractive index at 25 °C was found to be 1.38488 (to be compared with the literature values 1.3851 [18] and 1.3852 [19] at the same temperature).

3.2 — *CALIBRATION OF THE WIRE RESISTANCE*

The measuring technique used in this work monitors the resistance of the wire as a function of time. In order to find the temperature increase of the wire during the measurements, it is necessary to calibrate the resistance of the platinum wire as a function of temperature. This requires firstly the measurement of the wire resistance with a precision similar to that given by the automatic Wheatstone bridge, and secondly the knowledge of the wire temperature with sufficient accuracy for a reliable temperature resistance coefficient to be obtained. This is a very delicate procedure, well known to all who work in platinum resistance thermometry. We used a DANA 5900 digital multimeter and a four wire measurement with shielded two conductor cables, recommended for this kind of measurement. The precision of the measurement is of the order of 0.006 %, compared to the estimated accuracy of the automatic bridge of 0.05 %. The temperature was measured with a platinum resistance thermometer (TINSLEY TYPE 5187SA) which has an accuracy of ± 0.001 K, with the aid of an automatic bridge (Automatic Systems Laboratory A6) that measures $R_{pt}/(R_{st} + R_{pt})$, (R_{st} being a standard resistance of 100 Ω to one part in 10^6).

For the calibration the vessel was filled with helium. As temperature differences between the thermometer and the wire were expected, a measurement of the wire resistance at 20 °C immersed in n-heptane was done, and no difference was found.

Twenty-two data points were fitted to a quadratic polynomial between 8 °C and 41 °C and the result was

$$\frac{R_T}{R(273.16)} = 1 + 3.9985 \times \times 10^{-3} (T - 273.16) - 1.700 \times 10^{-6} (T - 273.16)^2 \tag{1}$$

with a variance of 0.04 Ω.

The percentage difference between experimental values (R_{exp}) and fitted values (R_{fit}) is presented in fig. 3 and a scatter of no more than 0.04 % is found. An analysis of the figure shows that a better calibration has been reached for temperatures above 24 °C where the residuals are smaller (of the order of 0.01 %). A better calibration for the temperatures below 24 °C will be tried in the near future.

3.3 — *OTHER EXPERIMENTAL PROBLEMS*

3.3.1 — TEMPERATURE STABILITY

After selecting the working temperature, we must wait for the temperature to stabilize inside the

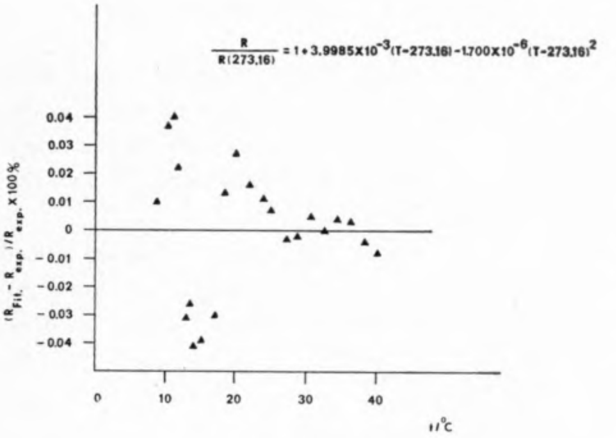

Fig. 3

Scattering of resistance fitted values as a function of temperature

vessel, ensuring that the temperature of the wire is the temperature measured with the platinum resistance thermometer. Experience shows that a waiting time of about $1\,{}^1/_2$ hour is enough to obtain a temperature stability of the order of $\pm$ 0.005 °C.

3.3.2 — TIME LAPSE BETWEEN RUNS

In order to meet the initial condition of uniform fluid temperature, it is necessary to estimate the time needed for the wire to reach again the bath temperature after a run; in fact, if the temperature of fluid which surrounds the wire changes by more than 0.005 K, the behaviour of the hot wire is markedly altered, and the reproducibility of consecutive runs is lost. By trial and error we have arrived at a time lapse between runs of the order of 2 minutes; experience shows that longer intervals will change the temperature of the bath by more than 0.005 K, and shorter intervals are obviously insufficient to allow for the wire to cool down.

4 — DATA CALCULATIONS

4.1 — *TEMPERATURE AND REFERENCE TEMPERATURE*

The simplest temperature profile that describes the temperature jump at the hot wire is the solution for the infinite line source of heat

$$\Delta T_o(a,\ t) = -\frac{q}{4\pi\lambda} E_i(-a^2/4Kt) \tag{2}$$

Assuming that the quantity $a^2/4Kt$ is sufficiently small, equation (2) can be put into the form

$$\begin{aligned} \Delta T_o(a,t) &= \frac{q}{4\pi\lambda}\left\{\ln\frac{4Kt}{a^2C} + \frac{a^2}{4Kt} + \dots\right\} \\ &= \frac{q}{4\pi\lambda}\left\{\ln\frac{4t^*}{C} + \frac{1}{4t^*} + \dots\right\} \end{aligned} \tag{3}$$

where $t^* = Kt/a^2$ is the reduced time.

Our instrument has been designed in such a way as to follow very closely the behaviour of a finite portion of an infinitely long and infinitely thin line source of constant heat flux q [5].

Recently HEALY and co-workers [7] refined the theory of the hot wire, firstly proposed by HAARMAN [3, 4]. Using a general perturbation technique, these authors arrived at several correcting terms which can be analysed separately or as a whole; these corrections are small (< 1 %) and since they were fully described elsewhere [4] they will only be briefly discussed here.

The thermal conductivity of the fluid at temperature T_r, λ_r, can be calculated from the slope of the temperature increase ΔT versus ln t diagram, according to the equation

$$\Delta T = \frac{q}{4\pi\lambda_r} \ln\left\{\frac{4(\lambda_o/\rho_o C_p)t}{a^2C}\right\} \tag{4}$$

where λ_0 and ρ_0 are the thermal conductivity and density of the fluid at bath temperature T_b and

$$\Delta T = \Delta T_W(t) + \sum_i \delta T_i \tag{5}$$

$\Delta T_W(t)$ is obtained from the wire resistance and the δT_i's are the temperature corrections.

The associated temperature T_r is obtained from the expression

$$T_r = T_b + \delta T_1{}^* \tag{6}$$

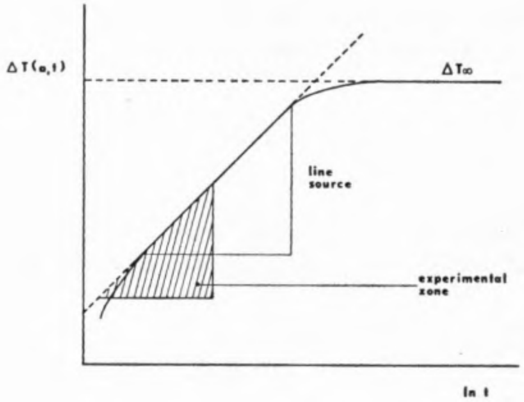

Fig. 4

Temperature increase of the wire as a function of logarithm of time

where the correction δT_1^* arises from the temperature dependence of fluid properties, ρC_p and λ.

4.2 — *CORRECTIONS*

4.2.1 — FINITE VALUES OF THE PHYSICAL PROPERTIES OF THE WIRE

Healy *et al.* [7] have derived an expression for the deviations of the measured temperature rise of the wire occuring as a result of its finite diameter, finite thermal conductivity and finite heat capacity.

$$\delta T_1 = a^2 \frac{(\rho C_p)_w - \rho C_p}{2\lambda t} \Delta T_w - \frac{q}{4\pi\lambda} \times \frac{a^2}{4Kt}\left(2 - \frac{K}{K_w}\right) - \frac{q}{8\pi\lambda_w} \tag{7}$$

The term $-q/4\pi\lambda_w$, which is very small, is independent of time and merely shifts the ΔT versus lnt diagram without changing the slope from which the thermal conductivity is calculated. The remaining terms are important at short times, but can be estimated with an error ~ 5 %. Thus, if we limit the application of such corrections to cases for which they are less than 1 % of the measured temperature rise, we may expect that the resulting departures from the linearity indicated by equation (4) will be of the order of ± 0.05 %.

4.2.2 — FINITE DIMENSIONS OF THE CELL

The existence of the cell wall causes the temperature rise in the fluid to be smaller than that for the ideal source solution. This fact is due to the heavy mass and high thermal conductivity of the cell walls (stainless steel).

Fischer [9] obtained the solution for the effect of the cell wall at a finite radius b; according to McLaughlin [8], for $b^* = b/a >> 1$, that solution can be approximated by

$$\Delta T(a,t) = \frac{q}{4\pi\lambda}\left\{2\ln b^* - 4 \times \sum_{n=1}^{\infty} \frac{\exp(-t^* g_n^2/b^{*2})}{\frac{g_n^2}{b^{*2}}\left\{\left(\frac{Y_1(g_n/b^*)}{Y_o(g_n)}\right)^2 - 1\right\}}\right\} \tag{8}$$

where g_n are the roots of $J_o(g_n) = 0$.

This temperature profile was calculated using the first 50 zeros of the Bessel function J_o but the results thus obtained do not agree with those of McLaughlin [8]. Our calculations generated negative temperature corrections δT_2

$$\delta T_2 = \Delta T_0(a,t) - \Delta T(a,t) \tag{9}$$

decreasing in absolute value when $t^* \rightarrow \infty$. These results are meaningless because δT_2 must be positive as we explained above and increase with increasing time.

An alternative to equation (8) is that of Fischer [9], valid for $b^* >> 1$ and $4t^* >> 1$

$$\Delta T(a,t) = \frac{q}{4\pi\lambda}\left\{2\ln b^* - 4 \times \sum_{n=1}^{\infty} \frac{\exp(-t^* g_n^2/b^{*2})}{\left(\frac{2}{\pi Y_o(g_n)}\right)^2 - \frac{g_n^2}{b^{*2}}}\right\} \tag{8a}$$

which gives the expected values for δT_2 for $t^* > 200$; these are plotted in fig. 5 for three values of b^*. We can easily see that $\delta T_2 \to 0$ as $t^* \to 0$ and $\delta T_2 \to 0$ as b^* becomes larger. For $b^* = 1000$ this correction is negligible until $t^* = 40000$, about ten times the value used in our experiments. This confirms previous results obtained by us [5] using the qualitative method due to HAARMAN [3]. In Table II of reference [5] it is shown that for $t^* \sim 50000$, the relative error in assuming that the medium has infinite dimensions is of the order of 10^{-6} for $b^* = 1000$.

Fig. 5 can be used for a careful choice of cell dimensions which eliminate this correction, because δT_2 is only a function of t^* and b^*, and for the transient regime $\Delta T_0(a,t) < \Delta T_\infty$ which gives $4t^*/C < b^{*2}$.

4.2.3 — OTHER CORRECTIONS

MCLAUGHLIN *et al.* [8] have shown that the viscous dissipation in liquids during the measurement will not exceed 0.01 % of the conduction heating. Using their results, a careful choice of the measurement time can be made in such a way as to prevent the onset of free convection.

The finite length of the wire implies that the temperature profile cannot be uniform along the entire length of the wire. To overcome this difficulty we have used, as shown in a previous report [5], a compensating wire as the other arm of the automatic bridge, and found that $R_L/R_S \sim 1.0001\ l_L/l_s$.

The last problem concern radiation. The simultaneous conduction and radiation in a participating medium has not yet been solved for coaxial cilinders in a transient regime. Recently MANI [11] attempted to solve the problem but his results have not yet become available. Meanwhile we are developing an approximate model which will allow us to correct the experimental results for radiative heat transfer in absorbing liquids. However, the results presented in this paper have not been corrected for radiation.

4.2.4 — VALUE OF δT_1^*

As explained above, the temperature at which the thermal conductivity of the fluid is measured (the so-called associated temperature T_r) is not the bath temperature, but must be corrected for the temperature dependence of fluid properties, namely ρC_p and λ. This problem has been solved for gases by HEALY *et al.* [7], and for liquids MCLAUGHLIN and PITTMAN [8] have developed a correction which is only applicable for a small increase of the wire temperature.

We have applied the results of HEALY *et al.* which assume that the fluid properties ρC_p and λ have a linear dependence on temperature, an assumption which for liquids is valid for even wider temperature ranges. The solution of the heat transfer equation under those boundary conditions gives a correction δT^*_1 to the reference temperature of the fluid, the so called bath temperature T_b

$$T_r = T_b + \delta T_1^* = T_b + \frac{1}{2}\{\Delta T(t_1) + \Delta T(t_2)\}$$

$$\rho_r = \rho(T_r,\ p_s)\ ;\ \lambda_r = \lambda_r(T_r)\ \text{at}\ p_s \tag{10}$$

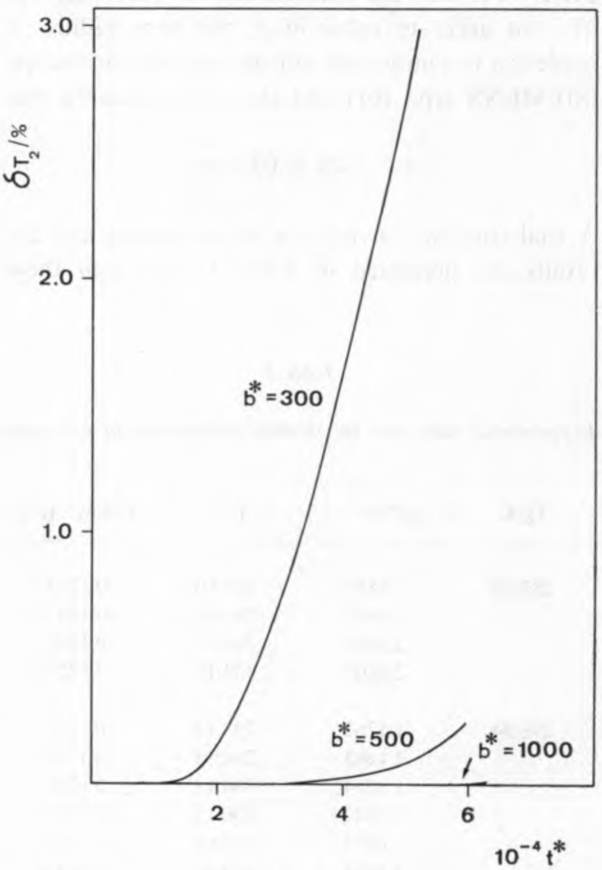

Fig. 5

Bounded medium correction for diffetent values of b and t**

Here t_1 and t_2 refer to the upper and lower limits of the time range within which ΔT is found to be a linear function of ln t to within 0.1 %. Typical values are $\Delta T(t_2) = 10K$, $\Delta T(t_1) = 5K$. The average slope of the ΔT vs ln t line in this range is then related to the thermal conductivity of the fluid at temperature T_r.

The experimental range used in our measurements ($t < 1s$) is compared in fig. 4 with the transient line source and the stationary temperature profile ΔT_∞, for the temperature jumps involved in our experiments, showing that the corrections are important only in the earlier part of the measurement.

5 — RESULTS

ΔT_w, δT_i and δT^*_1 were computed using a IBM 360 computer; the programs were written in FORTRAN IV. For the calculations, in particular for δT_1, an accurate value of a, the wire radius, is needed; *a* was measured with an electron microscope (SIEMENS type 101) and the value obtained was

$$a = 5.49 \pm 0.08 \ \mu m$$

A trial run was carried out for n-heptane and the results are presented in Table I. Although these are preliminary results, a comparison with the values obtained by other authors shows a reasonable agreement — Table II. There are reasons to believe that Pittman's are the most reliable available data for n-heptane; our values agree with his to 0.5 %, which is within the claimed experimental accuracy.

Table I

Experimental values for the thermal conductivity of n-heptane

T_b/K	q/Wm^{-1}	T_r/K	$\lambda/Wm^{-1}K^{-1}$
287.99	1.1874	293.60	0.1253
	1.8425	295.65	0.1242
	2.6303	298.15	0.1233
	2.6307	300.15	0.1227
293.04	1.1762	298.15	0.1235
	1.1493	298.15	0.1236
	1.8254	300.15	0.1229
	1.7842	300.15	0.1227
	2.6073	303.65	0.1217
	2.5471	303.65	0.1219
	2.5476	303.65	0.1220

Table II

Comparison of the available data for the thermal conductivity of n-heptane

T = 293.25 K	T = 303.15 K	Source
0.1244	0.1214	PITTMAN [13]
0.135	—	VILIM [14]
—	0.126	TSEDEBERG [15]
0.124	0.121	JOBST [20]
0.127	0.124	MISSENARD [16]
0.1254	*0.1219*	*Present work*

LIST OF SYMBOLS

Mathematical

$E_i(-x)$ — exponential integral
C = 1,781072
π = 3.14159
J_0 — Bessel function of first kind, order zero
Y_0, Y_1 — Bessel function of second kind, orders zero and one
g_n — n^{th} zero of J_0

Fluid and wire properties

a — wire radius
b — cell radius
$b^* = b/a$
C_p — specific heat at constant pressure
K — thermal diffusivity
l — wire length
P_s — saturation pressure
q — heat input per unit time and length
R_T — wire resistance at temperature T
t — time
$t^* = Kt/a^2$ — reduced time
ΔT_0 (a,t) — ideal wire temperature profile
ΔT (a,t) — real wire temperature profile
$\Delta T_W(t)$ — temperature profile obtained from bridge properties

T_r — temperature associated to the measured λ
T_b — bath temperature
T_∞ — steady state temperature
δT_i — wire temperature corrections
$\delta T_1{}^*$ — bath temperature correction
w — subscript referring to the wire properties
λ, λ_r — thermal conductivity of the liquid
ρ — density of the liquid

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RESUMO

Apresenta-se a medida da condutibilidade térmica do n-heptano à temperatura ambiente, utilizando a técnica do fio aquecido em regime transiente. O equipamento de medida foi projectado de forma a minimizar todos os efeitos secundários para que a condutibilidade térmica do líquido se possa obter do declive do acréscimo de temperatura num fio de platina de 10 μm de diâmetro em função do tempo. Escolha criteriosa da escala de medida permitiu uma eliminação de convecção livre; fizeram-se pequenas correcções devidas às propriedades físicas finitas do fio, à limitação do meio e à dependência de temperatura das propriedades do líquido. Os efeitos terminais do fio foram reduzidos a menos de 0,01 % com a utilização dum sistema de compensação, constituído por um fio curto de platina, colocado num dos braços adjacentes da Ponte de Wheatstone utilizada. Esta ponte regista os instantes em que a resistência do fio atinge 6 valores prefixados, utilizando um comparador electrónico e um relógio de 100 kHz com uma resolução de ± 10 μsegundos acoplados a um contador de seis canais. Os outros braços da ponte são formados por resistências de filme metálico, ultra-estáveis, para evitar variações de resistência.

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A POLUIÇÃO CAUSADA PELA INDÚSTRIA DO CONCENTRADO DE TOMATE. SUAS CAUSAS E MEIOS DE LUTA (1,2)

A indústria do concentrado de tomate tem um significado económico muito grande em Portugal, mas é igualmente uma causa importante de poluição hídrica. Apresenta-se o conjunto dos valores obtidos em três anos de colheitas em diferentes fábricas, tendo em vista a identificação das causas da poluição e a discussão dos resultados obtidos no tratamento por via biológica (bio-oxidação acelerada, seguida de tratamento químico complementar). Apresentam-se igualmente dados respeitantes à valorização de subprodutos e à reciclagem dos efluentes.

1 — INTRODUÇÃO

A influência das indústrias alimentares sobre o meio ambiente tem vindo a aumentar com o desenvolvimento deste sector da actividade económica, atingindo já, nalguns casos, situações preocupantes.

De acordo com Figueiredo (1973) as indústrias de alimentação, excluindo as indústrias das bebidas, provocam uma poluição equivalente a 6 413 353 habitantes-equivalentes, calculada na base de 54 g/dia de BOD_5, por habitante. Quanto às indústrias de bebidas o seu poder poluidor será de 2 583 992 habitantes-equivalentes. O conjunto representa, portanto, 8 997 345 habitantes-equivalentes, o que corresponde a 66 % do total de poluição atribuível ao conjunto das indústrias transformadoras existentes.

Admitindo que o encargo para se conseguir o tratamento integral dos esgotos, incluindo amortizações e manutenção, correspondente a um habitante-equivalente é de 100 escudos/ano, pode concluir-se que o prejuízo decorrente para a comunidade nacional será de cerca de 900 mil contos, correspondente à poluição das águas pelos efluentes não tratados.

Considerando, dentro do conjunto das indústrias alimentares, o sector das conservas de frutos e produtos hortícolas, verifica-se que ele corresponde a 1 002 079 habitantes-equivalentes, ou seja, que representa cerca de 7 % da poluição industrial total.

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(1) Presented at CHEMPOR' 75 held in Lisbon, 7-12 September 1975 at the Calouste Gulbenkian Foundation Center.
Papers presented at this International Chemical Engineering Conference can be purchased directly from Revista Portuguesa de Química (Instituto Superior Técnico, Lisboa 1, Portugal) at the following prices per volume sent by surface mail, postage included (in Portuguese Escudos):

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Environmental engineering	150
Management studies	150

This paper was presented at the Environmental engineering section.

(2) Trabalho realizado com a colaboração de: Reinaldo Mendes Barata, João Sarrico Damas, João Falcão, Leovigildo Duarte Henriques, Rui Soares Lopes, João Sevinate Pontes, Sabino Sousa Silvestre.

Pode pois concluir-se que, no contexto das agressões ecológicas provenientes do sector das indústrias transformadoras, as indústrias alimentares assumem grande relevância. Daí ser necessário encarar, com a maior urgência, a criação das infra-estruturas legais, executivas e laboratoriais, que possibilitem uma intervenção, activa e eficaz, dos serviços públicos no controle e combate aos prejuízos resultantes daquela actividade.

2 — A INDÚSTRIA DO CONCENTRADO DE TOMATE

A indústria do concentrado de tomate constitui, hoje em dia, um dos sectores mais evoluídos tecnologicamente, dentro do conjunto das indústrias ligadas à agricultura nacional. O valor de exportação excede 3 milhões de contos e a área cultivada de tomate é de cerca de 26 000 hectares.

O volume dos efluentes que a actividade desta indústria origina é muito elevado. Apesar de o grau de poluição ser relativamente diminuto comparado com o de outras indústrias (entre 300 e 500 ppm de BOD_5, em geral, embora na literatura se registem valores por vezes mais elevados), dado o volume de água utilizado, resulta daí uma carga poluente considerável.

Os efluentes das fábricas de concentrado de tomate podem ser caracterizadas pelos seguintes parâmetros:

a) Fácil biodegradabilidade, como se verifica pela proximidade dos valores de BOD_5 e de COD, facto que reflecte a natureza química dos poluentes (glúcidos, aminoácidos, proteínas, etc.).

b) Existência de uma fracção significativa de material em suspensão, facilmente retirável por crivagem, e que representa, em média, cerca de 25 % da carga poluente total.

c) Possibilidade de valorização dos resíduos crivados encaminhando-os, por exemplo, para a alimentação de bovinos ou suínos.

d) Carência em azoto e fósforo, que terão de ser adicionados ao efluente para que a depuração biológica seja eficiente.

e) Grande volume de efluentes diários, embora com um grau de poluição relativamente baixo (300-500 ppm de BOD_5, em média).

O lançamento destes efluentes em cursos de água ou albufeiras, sem qualquer tratamento, como era prática corrente no País, provoca alterações graves ao nível da fauna e da flora dos meios receptores.

O consumo de oxigénio aumenta de forma extremamente acentuada, podendo reduzir-se a zero o teor em dissolução nas águas. Esse fenómeno é aliás agravado por dois factores:

— carácter estival das emissões, correspondendo aos caudais mínimos e, portanto, ao mínimo de capacidade de autodepuração dos cursos de água;

— temperaturas elevadas, com consequente redução da capacidade de dissolução de oxigénio na água e, portanto, da capacidade de reoxigenação natural.

Nestas circunstâncias geram-se facilmente condições de anaerobiose, com fermentações pútridas e cheiros consequentes.

A fauna ictiológica é destruída e todo o bioma do ecossistema considerado é simplificado, em grau maior ou menor. A acumulação de detritos em decomposição e a modificação de cor das águas são manifestações exteriores que afectam especialmente as populações prejudicadas.

No «Simpósio sobre Poluição das Águas Interiores» realizado em Lisboa em 1970, afirmou-se que a indústria de concentrado de tomate era responsável pela impossibilidade de pesca temporária num percurso total de 20 km em 11 rios diferentes. Os troços poluídos tinham em média 2-3 km de comprimento, atingindo no máximo 5 km.

3 — MEDIDAS PREVENTIVAS DO COMBATE À POLUIÇÃO

3.1 — *ORIGENS DA POLUIÇÃO AO LONGO DO CIRCUITO FABRIL*

O tratamento dos efluentes da indústria de concentrado de tomate é possível, e não demasiado oneroso, desde que realizado dentro de determinados condicionalismos, como teremos ocasião de demonstrar.

Contudo é preferível evitar a ocorrência de determinadas situações a ter de remediar as consequências delas resultantes.

Tabela 1

Características da água de alimentação fabril, em unidades que recebem água de barragem e efectuam o seu tratamento (16 amostras)

Características da água de alimentação fabril	Amostras colhidas nas fábricas						Valores		
	A	E	F	G	H	J	Mínimo	Médio	Máximo
Temperatura (°C)	20–22	19–23	23–27	n.d.	n.d.	n.d.	19	22	27
pH	7,0–7,4	7,1–8,6	7,0–8,1	7,2	6,8	6,4	6,4	7,4	8,6
Sol. totais (ppm)	328–404	171–288	132–238	174	68	206	68	234	404
Sol. em suspensão (ppm)	3–16	0–4	2–24	3	0	18	0	7	24
Sol. em solução (ppm)	324–388	171–284	123–236	171	68	188	68	227	388
Mat. orgânica (ppm)	196–214	86–202	36–132	40	38	88	36	122	214
Cinzas (ppm)	132–208	85–176	34–120	134	30	118	30	112	208
BOD_5 (¹) (ppm)	36–110	30–35	31–42	24	90	49	24	50	110
COD (ppm)	45–125	18–49	11–56	26	104	58	11	49	125
BOD_5/COD	0,59–0,88	0,88–0,94	0,79–0,91	0,92	0,87	0,84	0,59	0,90	0,94

(¹) Diz respeito a 10 amostras unicamente.

Um dos meios de diminuir a carga poluente é exactamente determinar as origens da poluição e minimizar, a nível de circuito fabril, as perdas de matéria-prima que aí possam ocorrer.

Considerando o diagrama-tipo de uma fábrica de concentrado de tomate podem distinguir-se os seguintes tipos de efluentes nele individualizáveis (¹):

a) Água de condução e lavagem dos frutos, desde a recepção até às linhas de escolha.

b) Água das linhas de escolha.

c) Água proveniente dos passadores dos crivos.

d) Água proveniente da prensagem.

e) Água de lavagem do chão e do equipamento.

f) Água das colunas barométricas de condensação.

g) Água dos arrefecedores de latas.

No caso das fábricas onde se produz também tomate pelado há que considerar a água residual da pelagem, e dentro desta há que distinguir a pelagem mecânica da pelagem química.

Em relação a diversas fábricas de concentrado de tomate foi possível realizar análises de efluentes parciais, de modo a determinar o grau de poluição relativo de cada um deles.

Designaram-se pelas letras A a J as unidades fabris onde foram colhidas amostras, referindo-se nos quadros seguintes as diversas fábricas pelas letras respectivas.

As amostras, nas quais se determinou, imediatamente após a colheita, a temperatura e o pH, foram transportadas em câmara refrigerada para o laboratório onde se realizaram, em duplicado, as determinações seguintes:

— *Sólidos totais* — por evaporação em banho-maria de 50 cm³ do efluente e secagem a 110 °C, até peso constante.

— *Sólidos em suspensão* — por filtração sob sucção, através de cadinho Goosh n.º 3, seguida de secagem na estufa a 110 °C, até peso constante.

— *Sólidos em solução* — por diferença (Sólidos em solução = Sólidos totais — Sólidos em suspensão).

— «*Matéria orgânica*» — por diferença (Matéria orgânica = Sólidos totais — Cinzas) (²).

(¹) Além destes efluentes, ligados ao processamento do tomate, existirão ainda:

a) Resíduos de nafta, provenientes das descargas de secador e dos geradores de vapor.

b) Óleos e massas lubrificantes, das oficinas de manutenção fabris.

c) Efluentes das instalações sanitárias.

(²) Note-se que sob a rubrica «Matéria orgânica» se incluem substâncias inorgânicas decomponíveis abaixo de 750 °C, nomeadamente carbonatos e bicarbonatos.

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NOTA

A exemplo do que se passou com o volume anterior da Revista Portuguesa de Química, também este se publica com grande atraso em relação às datas de recepção dos originais. Encontram-se já publicados os volumes 18 (n.os 1 a 4) e 19 (n.os 1 a 4) contendo os trabalhos apresentados ao V Simpósio Ibero-Americano de Catálise.

NOTE

As happened with the previous volume of the Revista Portuguesa de Química this is also published much later than its printed date.

Volumes 18 (nos. 1-4) and 19 (nos. 1-4) containing the papers presented to the Fifth Iberoamerican Symposium on Catalysis which was held in July 1976, in Lisbon, have already been published.

Tabela 2

Características da água de alimentação fabril em unidades que recorrem a perfurações (18 amostras)

Características da água de alimentação fabril	Amostras colhidas nas fábricas				Valores		
	B	C	D	I	Mínimo	Médio	Máximo
Temperatura (°C)	19–25	17–24	19–24	n.d.	17	22	25
pH	7,2–7,6	7,2–7,5	6,2–7,0	7,0	6,2	7,0	7,6
Sol. totais (ppm)	124–242	204–352	340–564	135	124	296	564
Sol. em suspensão (ppm)	1–31	5–13	0–27	12	0	10	31
Sol. solúveis (ppm)	114–234	196–347	335–564	123	114	286	564
Mat. orgânica (ppm)	1–78	86–166	146–342	60	1	149	342
Cinzas (ppm)	106–179	104–218	76–296	75	76	147	296
BOD_5 (¹) (ppm)	4–7	10–32	23–40	12	4	20	40
COD (ppm)	5–12	8–37	21–65	18	5	24	65
BOD_5/COD	0,62–0,70	0,83–0,86	0,82–0,95	0,67	0,62	0,79	0,95

(¹) Diz respeito a 11 amostras unicamente.

— *Cinzas* — por incineração em mufla a 750 °C.

— *COD* — por oxidação a quente com uma solução de dicromato de potássio, titulando o excesso pela solução de Sal de Mohr, usando a ferroína como indicador.

— *BOD_5* — por incubação a 20 °C na escuridão durante 5 dias, doseando o oxigénio dissolvido pelo método WINCKLER.

Nas Tabelas 1 e 2 apresentam-se dados referentes a 34 amostras de água de alimentação fabril colhidas em 10 fábricas diferentes. Na Tabela 1 resumem-se os valores respeitantes a unidades fabris que utilizam água de barragem tratada, no seu circuito fabril. O tratamento da água praticado consiste, em geral, numa adição de sulfato de alumínio e hidróxido de cálcio, seguida de filtração em filtro de areia, após floculação. A clorinação é generalizada. Na Tabela 2 pelo contrário apresentam-se dados respeitantes a fábricas que utilizam água proveniente de perfurações na alimentação do circuito fabril. De realçar a melhor qualidade da água desta segunda origem, na generalidade dos casos considerados.

Tabela 3

Características de efluente proveniente das linhas de lavagem (14 amostras)

Características do efluente	Amostras colhidas nas fábricas					Valores		
	B	C	D	E	F	Mínimo	Médio	Máximo
Temperatura (°C)	32–33	27–32	22–32	19–20	27	19	27	33
pH	7,2	6,9	6,9–7,1	6,8–7,0	7,4–7,8	6,8	7,2	7,8
Sol. totais (ppm)	370–504	416–666	490–630	300–436	398–570	300	473	666
Sol. em suspensão (ppm)	30–62	22–111	19–62	11–66	38–81	11	54	111
Sol. em solução (ppm)	340–451	387–553	451–569	289–370	360–489	289	419	569
Mat. orgânica (ppm)	154–290	222–384	216–382	134–320	270–430	134	277	430
Cinzas (ppm)	168–216	114–298	160–342	116–166	128–140	114	196	342
BOD_5 (ppm)	233–360	333–502	174–250	402–415	271–312	174	294	502
COD (ppm)	284–428	385–594	235–353	454–468	319–361	235	349	594
BOD_5/COD	0,82–0,87	0,85–0,87	0,71–0,84	0,89	0,86	0,71	0,83	0,89

Tabela 4

Características dos efluentes provenientes dos grupos de refinação (16 amostras)

Características do efluente	Amostras colhidas nas fábricas						Valores		
	A	B	C	D	E	F	Mínimo	Médio	Máximo
Temperatura (°C)	20–23	23–28	28	26–41	24–30	28	20	28	41
pH	4,7–6,6	5,8–6,5	6,3	4,1–4,8	3,9–5,3	5,0	3,9	5,1	6,6
Sol. totais (ppm)	632–4926	1394–4484	2794	6552–18394	4154–5580	7676	632	6477	18394
Sol. em suspensão (ppm)	194–3097	769–2699	574	4667–11117	1165–3314	4096	194	3598	11117
Sol. em solução (ppm)	312–1829	625–1785	2220	2415–8027	2274–2989	3580	312	2879	8027
Mat. orgânica (ppm)	376–4564	1113–4098	2382	6096–17226	3522–5274	7268	376	5987	17226
Cinzas (ppm)	256–362	202–386	412	556–1168	306–632	408	202	490	1168
BOD_5 (ppm)	345–5104	2801–4000	3002	7984–13005	4997–5601	10498	345	5906	13005
COD (ppm)	401–6026	3349–4851	3746	8641–14240	6124–6737	12339	401	7037	14240
BOD_5/COD	0,76–0,86	0,82–0,84	0,80	0,77–0,92	0,82–0,83	0,85	0,76	0,84	0,92

Na Tabela 3 apresentam-se os valores obtidos na análise de 14 amostras colhidas em 5 fábricas diferentes e representando o efluente resultante da lavagem dos frutos nas linhas de escolha. Como se pode verificar a poluição daí decorrente é considerável. Admitindo que uma linha de escolha consome cerca de 10 m³ de água por hora (¹) a carga resultante será de 2,94 g de BOD_5, ou seja, de 1,3 equivalente-habitante/dia/linha.

Na Tabela 4 resumem-se os dados respeitantes à análise de 16 amostras de efluente dos grupos de refinação. É evidente, da consulta dos valores disponíveis, que ele constitui a mais grave origem de poluição a nível destas unidades fabris. Mesmo para um volume da ordem de 1 m³/hora a carga poluente horária será em média de 59,06 g de BOD_5, ou seja, de 26,2 equivalentes-habitante/dia. Há pois todo o interesse em minimizar a carga poluente daqui resultante, o que se traduz, aliás, por um aumento do rendimento fabril, a par de uma diminuição do poder poluidor da fábrica.

Nalgumas fábricas recorre-se a prensas horizontais, de compressão por vezes reduzida, para diminuir o teor em humidade de repiso, antes de entrar no secador. A poluição daí resultante é considerável, como se pode ver na Tabela 5. Assinale-se ainda a diferença marcada entre as amostras de cada uma das fábricas, motivada pelas características das prensas existentes e sua condução em condições laborais.

O efluente que quantitativamente mais representa em termos de volume é a água de condensação das colunas barométricas. O seu grau de poluição é contudo diminuto e daí a sua importância como factor de diluição dos outros subefluentes mais poluidores. De assinalar que nalgumas amostras o grau de poluição é um pouco mais elevado, o que reflecte contaminações ao longo do seu percurso, que se podem considerar evitáveis, desde que a laboração seja correctamente conduzida. Este aspecto é também importante para fins de rendimento, dado que a contaminação usual será o arraste de gotículas de sumo. Na Tabela 6 apresentam-se os valores correspondentes a 15 amostras colhidas em 5 fábricas diferentes.

Nas tabelas anteriores apresentaram-se, portanto, dados relativos às causas de poluição mais importantes que se podem individualizar para efeitos de amostragem, nas unidades dedicadas ao fabrico do concentrado de tomate. Convém referir ainda o caso das linhas de pelagem mecânica ou química, eventualmente existentes, e elas também causas de poluição significativa. Na Tabela 7 apresentam-se os dados recolhidos e respeitantes a linhas de ambos os tipos. Como se pode verificar a pelagem mecânica conduz a um grau de poluição mais elevado. Além disso o elevado pH do efluente das linhas de pelagem química neutraliza, ao menos em parte, a acidez devida aos restantes efluentes, o que se traduz por valores mais elevados do pH do efluente final.

(¹) Pode nalguns equipamentos atingir 15 m³/hora.

Tabela 5

Características dos efluentes provenientes de prensas horizontais (6 amostras)

Características do efluente	Amostras colhidas nas fábricas		Valores		
	B	E	Mínimo	Médio	Máximo
Temperatura (°C)	21–24	36–52	21	32	52
pH	5,8–7,0	3,8–4,4	3,8	5,3	7,0
Sol. totais (ppm)	724–3562	8630–64986	724	23552	64986
Sol. em suspensão (ppm)	165–1556	5150–40670	165	9551	40670
Sol. em solução (ppm)	559–2006	3480–24316	559	14001	24316
Mat. orgânica (ppm)	466–3208	8010–59622	466	21321	59622
Cinzas (ppm)	196–354	620–6592	196	2231	6592
BOD_5 (1) (ppm)	2120–3456	15879–17425	2120	8376	17425
COD (ppm)	2568–4021	11780–20354	2568	10148	20354
BOD_5/COD	0,83–0,86	0,85–0,86	0,83	0,85	0,86

(1) Diz respeito apenas a 5 amostras.

Finalmente na Tabela 8 apresentam-se os valores obtidos a partir de 28 amostras diferentes, recolhidas em 6 fábricas e ao longo de 3 campanhas, que permitem caracterizar o esgoto geral de uma fábrica de concentrado de tomate. Como é evidente são numerosas as causas de variação de poder poluidor de caso para caso. Basta recordar, entre outras:

— o quantitativo de fruto laborado;
— o estado de conservação dos frutos;
— o tipo de maquinaria usada;
— a condução das operações fabris;
— a qualidade da água de alimentação;
— o tipo e qualidade dos produtos fabricados; etc.

De qualquer modo verifica-se uma razoável proximidade dos valores obtidos para a maior parte das características analisadas que, como se pode verificar, se ajustam aos parâmetros indicados, a título genérico, no parágrafo 2.

3.2 — *MEIOS DE REDUZIR A POLUIÇÃO*

É importante assinalar que os meios de reduzir a poluição são, em geral, também meios de aumentar

Tabela 6

Características da água de condensação das colunas barométricas (15 amostras)

Características da água de condensação das colunas barométricas	Amostras colhidas nas fábricas					Valores		
	A	C	D	E	F	Mínimo	Médio	Máximo
Temperatura (°C)	27–34	33–44	22–46	22–28	41	22	34	46
pH	7,0–7,3	7,0–7,4	7,0–7,8	7,3–8,6	8,3	7,0	7,5	8,6
Sol. totais (ppm)	302–412	174–222	408–514	280–300	234	174	336	514
Sol. em suspensão (ppm)	7–16	4–31	0–31	0–19	37	0	12	37
Sol. em solução (ppm)	295–396	163–218	405–513	267–300	197	163	324	513
Mat. orgânica (ppm)	102–166	30–74	248–338	140–196	128	30	181	338
Cinzas (ppm)	198–280	100–190	106–190	90–160	106	90	155	280
BOD_5 (1) (ppm)	40–122	52–147	14–124	104	50	14	86	147
COD (ppm)	45–168	61–201	18–145	114–165	56	18	110	201
BOD_5/COD	0,62–0,89	0,69–0,85	0,79–0,93	0,90	0,89	0,62	0,80	0,93

(1) Diz respeito a 12 amostras unicamente.

Tabela 7

Características de efluentes de linhas de pelagem

Características do efluente das linhas de pelagem	Pelagem mecânica		P. química
	Amostras colhidas nas fábricas		
	D	E	D
Temperatura (°C)	23	23	20
pH	6,7	4,8	8,6
Sol. totais (ppm)	714	778	502
Sol. em suspensão (ppm)	97	124	94
Sol. em solução (ppm)	617	654	408
Mat. orgânica (ppm)	382	552	190
Cinzas (ppm)	332	226	312
BOD_5 (ppm)	502	2360	114
COD (ppm)	613	2850	195
BOD_5/COD	0,82	0,83	0,58

o rendimento fabril, ou de melhorar a qualidade do produto final. Há pois um múltiplo benefício, aspecto que torna extremamente aliciantes as iniciativas tomadas neste sentido.

Em primeiro lugar há que atender à água de alimentação fabril. A qualidade desta é, como se provou pelos valores das Tabelas 1 e 2, muito diferente de fábrica para fábrica. Basta recordar que o BOD_5 médio encontrado, no caso de a água ser proveniente de furos, foi de 20 ppm, enquanto no caso de água de barragem tratada subiu para 50 ppm. Daqui resulta que uma fábrica que consuma, por exemplo, 400 m^3/h teria, no segundo caso, uma carga poluente horária extra de 12 kg de BOD_5, ou seja de 222 equivalentes-habitante.

O tratamento da água de alimentação fabril é pois um primeiro passo, de decisiva importância, na minimização da carga poluente.

Um segundo aspecto a atender diz respeito ao estado em que os frutos se encontram no início da laboração. As condições de apanha e de transporte, as características da zona de parque, o tempo de demora entre a apanha e a laboração, o estado fitossanitário dos frutos são factores que, *a priori*, assumem a maior importância. Basta atender aos valores da Tabela 3 e, mais concretamente ainda, aos valores extremos do BOD_5 nele registados. Calculou-se já que, para o valor médio encontrado, a carga poluente horária, para uma linha de escolha alimentada com 10 m^3/hora de água, era de 2,94 g de BOD_5. Mas os valores extremos seriam de 1,74 g e 5,02 g, respectivamente, ou seja de 0,77 e 2,23 equivalentes-habitante/dia. Uma variação deste tipo, de simples para o triplo, muito embora determinada em parte pela altura da campanha em que é efectuada, reflecte também a possibilidade de, neste domínio, se conseguirem progressos interessantes.

Embora não se disponham de dados referentes à poluição causada pelo transporte hidráulico de

Tabela 8

Características do esgoto geral (28 amostras)

Características do esgoto geral	Amostras colhidas nas fábricas						Valores		
	A	B	C	D	E	F	Mínimo	Médio	Máximo
Temperatura (°C)	24–31	31–32	28–38	21–33	19–25	26–28	19	27	38
pH	6,5–7,0	6,4–6,8	6,8–7,2	6,5–7,8	5,5–7,0	6,8–7,5	5,5	6,8	7,5
Sol. totais (ppm)	430–584	768–857	266–650	574–1492	444–704	508–750	266	629	1492
Sol. em suspensão (ppm)	28–99	132–170	14–162	50–725	81–196	58–79	14	140	725
Sol. em solução (ppm)	372–485	598–700	165–575	372–767	350–555	450–671	165	489	767
Mat. orgânica (ppm)	232–368	520–676	94–444	362–1030	346–508	364–604	94	420	1030
Cinzas (ppm)	192–216	156–248	108–206	128–496	98–206	144–146	98	209	496
BOD_5 (1) (ppm)	132–345	305–530	270–300	340–604	380–698	181–425	132	374	698
COD (ppm)	154–428	386–604	90–359	359–697	458–786	206–496	90	422	786
BOD_5/COD	0,81–0,86	0,79–0,88	0,81–0,85	0,84–0,92	0,83–0,89	0,86–0,88	0,79	0,86	0,92

(1) Diz respeito a 20 amostras.

frutos transportados a granel é evidente que nessas condições a situação se agrava sensivelmente deste ponto de vista. As injúrias sofridas pela epiderme dos frutos, com a consequente difusão de sumo, vão certamente baixar o pH e aumentar o teor em sólidos solúveis do efluente quando comparado com processos menos traumatizantes, como os que tradicionalmente se utilizavam. Face a uma opção que será ditada por razões económicas há que adiantar que ela se traduz forçosamente pela diminuição do rendimento em termos de Matéria-prima / /Produto transformado e pelo aumento do poder poluidor da fábrica. De qualquer modo há que procurar diminuir essas perdas através de:

- limitação da carga transportada a granel (nomeadamente da altura da pilha de frutos);
- limitação das injúrias causadas pela maquinaria (descarga, tapetes transportadores, etc.);
- eventual aproveitamento do sumo escorrido para o atrelado, retido por uma protecção de polietileno e sugado após a descarga dos frutos (1).

Uma das causas de poluição mais graves é, como se disse, o efluente dos grupos de refinação, cujos valores de BOD_5 são extremamente elevados. A análise da Tabela 4 mostra-nos, desde logo, que a variação é muito acentuada de amostra para amostra. Isso reflecte, ao menos, em parte, a maior ou menor afinação dos crivos, nos casos em que tal é possível. Este é pois, desde logo, um aspecto a atender e a vigiar cuidadosamente. Mas tem muito maior interesse a utilização de uma prensa vertical, de elevado poder de compressão, que permite:

- reduzir substancialmente o teor em humidade de repiso, facilitanto a sua ulterior secagem;
- recuperar grande quantidade de sumo que pode ser enviado para o circuito de concentração.

O aumento de rendimento daí resultante foi, nalgumas unidades que assim fizeram, muito substancial, atingindo nalguns casos quase 10 %. O significado económico e ecológico deste procedimento é, evidentemente, muito importante.

Aliás também por esta via se pode eliminar o efluente proveniente de prensas horizontais, cujas características se indicaram na Tabela 5.

Já atrás se referiu, a propósito da água de condensação das colunas barométricas, a necessidade de se evitarem contaminações com substâncias poluentes (sumo de tomate), que podem ocorrer ao verificar-se uma modificação brusca das condições de pressão. Aliás nalgumas unidades a água de condensação é arrefecida e clorinada, reutilizando-se por exemplo no transporte hidráulico e na pré-lavagem dos frutos.

Como exemplo apresentam-se os valores médios dos parâmetros analíticos respeitantes a três amostras de água de condensação clorinada e a três amostras de água de alimentação fabril, colhidas simultaneamente, numa unidade de fabrico de concentrado de tomate:

	Água de condensação clorinada	Água de alimentação fabril (furo)
Temperatura	28 °C	24 °C
pH	7,4	7,4
Sólidos totais	297 ppm	160 ppm
Sólidos em suspensão	9 ppm	13 ppm
Sólidos em solução	288 ppm	147 ppm
«Matéria orgânica»	147 ppm	8 ppm
Cinzas	150 ppm	152 ppm
BOD_5	81 ppm	5 ppm
COD	96 ppm	8 ppm
BOD_5/COD	0,84	0,66

Muito embora a qualidade da água recuperada seja francamente pior que a da água de alimentação fabril (aliás muito boa), a economia hídrica daí resultante era já sensível (27 %), tendo aumentado ainda mais com a melhoria do sistema de arrefecimento.

Finalmente, e no caso de existirem linhas de pelagem, há que referir a menor carga poluente da pelagem química, correctamente conduzida e controlada, em comparação com a pelagem mecânica, sem entrar em conta com outros aspectos ligados à economia de matéria-prima e de mão-de-obra, também a considerar.

Há pois uma margem de variação muito grande na carga poluente gerada por uma unidade de fabrico de concentrado de tomate. Para um efluente

---

(1) A escolha de variedades de tomateiro resistentes é uma metodologia genérica indispensável.

com o caudal de 400 m^3/hora teríamos assim por hora de trabalho efectivo:

	BOD_5	Equivalentes-habitante
Mínimo	52,8 kg	978
Médio	149,6 kg	2770
Máximo	279,2 kg	5171

Ressalvando a influência da qualidade da matéria-prima e do transporte até ao parque, resta ainda uma larguíssima margem de manobra no sentido de minimizar as perdas de matéria-prima ao longo do circuito fabril, com consequente aumento da produtividade e redução do poder poluente dos efluentes.

4 — DEPURAÇÃO BIOLÓGICA DOS EFLUENTES

4.1 — *FUNDAMENTOS DO PROCESSO*

A depuração biológica de um efluente engloba em si todo um conjunto de processos distintos, conduzindo à eliminação ou diminuição da carga poluente mediante a intervenção de microrganismos. Esses microrganismos, desde que as condições ambientais lhes sejam favoráveis, entram num processo de desenvolvimento acelerado, à custa dos poluentes orgânicos presentes. Os poluentes inorgânicos podem ser, ao menos em parte, igualmente afectados pelas reacções bioquímicas, ou floculados, no decurso ou como consequência dessas mesmas reacções.

Como é evidente procura-se na depuração biológica reproduzir, activando-a, a situação desempenhada pelos decompositores nos ecossistemas naturais.

O objectivo é pois a conversão das substâncias poluentes em solução e/ou suspensão em materiais insolúveis removíveis, gases e água.

Um dos métodos de depuração biológica que tem sido utilizado no tratamento de efluentes de indústrias alimentares é a chamada lagunagem arejada, que consiste, em traços muito gerais, na criação de uma lagoa onde a capacidade de auto-depuração seja maximizada pela adição exógena do oxigénio e nutrientes necessários a uma intensidade metabólica elevada. Trata-se de um método que tem a seu favor as vantagens seguintes:

— modicidade de preço;
— eficiência aceitável;
— facilidade de exploração.

Em relação às indústrias alimentares, concretamente à indústria de concentrado de tomate, estes aspectos são relevantes, dado o seu carácter sazonal e a necessidade de limitar os investimentos ao mínimo aceitável.

Foi este o método adoptado como base e daí referir-se a fundamentação teórica seguinte às condições existentes numa lagoa de bio-oxidação forçada.

Em presença de oxigénio dissolvido os microrganismos utilizam parte das substâncias orgânicas presentes como fonte de energia, sendo outra parte assimilada com formação de protoplasma, quer através do aumento do número de células, quer através do incremento de massa dessas células.

Uma vez esgotados os nutrientes presentes outros microrganismos intervêm, estes de dimensões sucessivamente maiores, até se atingir uma fase em que a floculação é possível, separando-se a matéria orgânica insolubilizada por decantação.

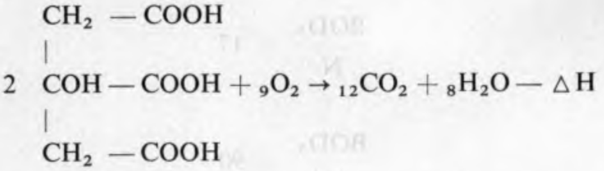
Há pois três fases a considerar neste complexo processo: uma fase que corresponde à bio-oxidação das substâncias orgânicas presentes, uma outra fase de assimilação dos nutrientes, com síntese de protoplasma, e uma terceira fase de auto-oxidação, correspondente à respiração endógena.

Considerando uma substância orgânica terciária $C_xH_yO_z$ a sua oxidação processar-se-á segundo a equação genérica

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2 \xrightarrow{\text{Enzimas}} x\,CO_2 + \frac{y}{2} H_2O - \Delta H$$

Deste modo se mobiliza a energia necessária às sínteses que constituem a fase assimilatória, além de que parte importante das substâncias solúveis é eliminada sob a forma de CO_2 e H_2O.

No caso do efluente de uma fábrica de concentrado de tomate poderíamos concretizar a equação para o caso do ácido cítrico escrevendo



$$\begin{array}{ll} & CH_2 - COOH \\ & \quad | \\ 2 & COH - COOH + {}_9O_2 \rightarrow {}_{12}CO_2 + {}_8H_2O - \Delta H \\ & \quad | \\ & CH_2 - COOH \end{array}$$

A energia livre assim tornada disponível vai permitir a síntese de protoplasma. A composição química do protoplasma, variável embora com as espécies e com as condições de nutrição, é, de uma forma aproximada, a seguinte:

50 a 55 % de carbono
25 a 30 % de oxigénio
≃ 10 % de azoto
6 a 7 % de hidrogénio
≃ 1 % de fósforo

existindo ainda quantidades menores de outros elementos, nomeadamente de enxofre, magnésio, cálcio, sódio, ferro, cobre, zinco, manganésio, etc. Daí o admitir-se uma fórmula química média para o protoplasma que, segundo alguns autores, será

$$C_5H_7NO_2$$

Não há aliás acordo, havendo outros que propõem $C_8H_{12}N_2O_3$, ou até $C_{118}H_{170}N_{17}O_{51}P$. Segundo McKinney pode detalhar-se essa composição até ao nível de grandes grupos e assim indica esse autor:

— para as bactérias	$C_5H_7NO_2$
— para os fungos	$C_{10}H_{17}NO_6$
— para as algas	$C_{5,7}H_{9,8}NO_{2,3}$
— para os protozoários	$C_7H_{14}NO_3$

A assimilação global correspondente à assimilação, isto é, à síntese do protoplasma, pode pois escrever-se sob a forma

$${}_n(C_xH_yO_z) + {}_nNH_3 + {}_n\left(x + \frac{y}{4} - \frac{z}{2} - 5\right) O_2 \rightarrow$$

$$\rightarrow (C_5H_7NO_2)_n + {}_{n(x-5)}CO_2 + \frac{n}{2}(y-4)\, H_2O \pm \Delta H$$

No caso do ácido cítrico teremos

$${}_nC_6H_8O_7 + {}_nNH_3 - \frac{n}{2}\, O_2 \rightarrow (C_5H_7NO_2)_n +$$

$$+ {}_nCO_2 + {}_{2n}H_2O$$

Note-se que no decurso da assimilação o balanço de oxigénio é positivo, dado o carácter oxigenado da molécula do ácido cítrico.

A última fase do ciclo metabólico depurativo será a respiração endógena, que se pode traduzir pela equação

$$(C_5H_7NO_2)_n + {}_{5n}O_2 \rightarrow$$

$$\rightarrow {}_{5n}CO_2 + {}_{2n}H_2O + {}_nNH_3 - \Delta H$$

Desta equação se deduz que a desassimilação de protoplasma exige uma relação O_2/Protoplasma igual a

$$\frac{{}_5O_2}{C_5H_7NO_2} \simeq 1{,}42$$

isto é, por 1 g de protoplasma a auto-oxidar é necessário fornecer 1,42 g de oxigénio exógeno.

Em resumo pode pois dizer-se que a depuração biológica se pode traduzir por uma equação genérica do tipo

Subs. poluentes + Microrganismos + Oxigénio →
→ Mais microrganismos + CO_2 + H_2O

A variação do BOD_5 ao longo do período de depuração nas lagoas de bio-oxidação forçada tem sido descrita a partir de diversas expressões matemáticas. Em primeira aproximação pode dizer-se que segue a evolução definida por

$$\frac{BOD_5 \text{ inicial}}{BOD_5 \text{ final}} = 1 + Kt$$

sendo t expresso em dias e sendo K uma constante, função dos parâmetros experimentais em causa.

4.2 — *ESQUEMA DA INSTALAÇÃO-TIPO ADOPTADA*

Embora cada instalação constitua um caso único, apresentando características específicas bem definidas, pode dizer-se que, de uma forma genérica, a instalação de bio-oxidação forçada proposta compreende os seguintes elementos:

a) Um crivo rotativo, destinado a recuperar parte do material em suspensão, nomeadamente pedaços de frutos, frutos rejeitados, folhagem, etc.

b) Um sistema de lagoas intercomunicantes, com as dimensões necessárias para assegurar o tempo de passagem necessário para que a depuração atinja os níveis exigidos.

c) Um sistema de fornecimento e distribuição de ar comprimido, capaz de fornecer a quantidade de oxigénio necessária aos processos metabólicos decorrentes.

d) Um sistema de distribuição dos nutrientes que é necessário adicionar para que o crescimento microbiano se processe em condições óptimas.

e) Uma lagoa de floculação, reforçada esta pela adição de sulfato de alumínio ou de outro agente floculante equivalente.

f) Um sistema de distribuição de cloro, no final do processo, de modo a evitar contaminações microbianas indesejáveis no meio receptor.

Passando à análise de cada um destes elementos, uma palavra acerca de crivagem preliminar. O crivo adoptado, de fabrico nacional, é rotativo, com cerca de 3 m de comprimento e 1,4 de diâmetro, recoberto com malha de 1,5 mm. A fim de determinar a eficiência desta operação efectuaram-se colheitas, antes e depois da instalação de crivagem, caracterizando-se, seguidamente, os dois efluentes. As médias de 8 ensaios, efectuadas em fábricas diferentes e em diferentes alturas de campanha, podem ser resumidas da seguinte maneira:

	Variação após crivagem
pH	— 0,3 unidades
Sólidos totais	— 18,4 %
Sólidos em suspensão	— 33,7 %
Matéria orgânica	— 19,8 %
BOD_5	— 21,2 %
COD	— 17,9 %

A fase seguinte é a de bio-oxidação forçada, para o que se torna necessário:

a) Corrigir a composição química do efluente, pela adição, nomeadamente, de azoto e de fósforo.

b) Adicionar oxigénio, de modo a compensar o consumo inerente à depuração microbiana.

De acordo com a bibliografia disponível as relações óptimas entre o BOD_5 e os teores em N e P são, respectivamente,

$$\frac{BOD_5}{N} = 17$$

$$\frac{BOD_5}{P} = 90$$

Os teores naqueles elementos presentes de efluente crivado são inferiores àqueles valores, pelo que há que corrigi-los recorrendo para tal a uma suspensão de adubos comerciais, de modo a minimizar o preço de custo e adicionar ainda alguns outros elementos, cuja presença é conveniente para os fins em vista.

Uma vez feita a análise de diversas amostras adoptou-se como base a adição de 3,8 mg de azoto e de 1,5 mg de P_2O_5 por litro. O azoto foi fornecido sob a forma de ureia e o P_2O_5 na forma de superfosfato de cal a 18 %. Quanto à quantidade de oxigénio foi calculada com base nos valores obtidos experimentalmente respeitantes à sequência de reacções metabólicas admitidas em 4.1.

Assim a oxidação de matéria orgânica corresponde a um consumo médio de 0,4 g de oxigénio por 1 g de matéria orgânica presente.

A biossíntese celular, por sua vez, processa-se com uma eficiência da ordem dos 50 % na conversão Matéria orgânica-Protoplasma.

Finalmente a respiração endógena corresponde ao consumo de 1,42 g de oxigénio por 1 g de protoplasma a auto-oxidar.

Como resultado da aplicação desses coeficientes ao efluente em causa pode calcular-se o consumo de oxigénio correspondente, o qual é convertido em volume de ar a injectar, tendo em conta a eficiência dessa mesma injecção, função de diversos factores, tais como, o diâmetro das bolhas, a altura de água, a pressão manométrica do compressor, etc.

Após a bio-oxidação torna-se necessário adicionar um agente floculante, de modo a aumentar a taxa de separação da matéria orgânica insolubilizada do meio líquido. O produto usado foi o sulfato de alumínio, o qual, em meio aquoso, se dissocia dando origem a

$$Al_2(SO_4)_3 \rightarrow {}_2Al^{+++} + {}_3SO_4^{=}$$

Os iões Al^{+++} vão reagir com os iões de carga negativa e conduzem à floculação das partículas em suspensão, nomeadamente dos organismos de maiores dimensões, tais como protozoários, algas, etc.

Muito embora o processo esquematizado conduza obviamente a resultados óptimos quando funcionando em contínuo, especialmente pela adaptação mais profunda da microfauna aos poluentes, realizou-se um ensaio em descontínuo, de modo a caracterizar a eficiência de cada uma destas fases e sua progressão no tempo. Como é evidente os resultados obtidos têm de considerar-se como um mínimo, uma vez que não se procedeu à prévia adaptação dos microrganismos e que se trabalhou em descontínuo. Contudo a análise dos valores contidos na Tabela 9 mostra-nos que a redução de COD obtida após 22 horas de ensaio foi de 58,5 %, partindo de um efluente artificial com 234 ppm e obtido por diluição de concentrado de tomate, de modo a reproduzirem-se condições de laboração usuais.

É pois de prever que o funcionamento em contínuo, com adaptação enzimática e por períodos mais longos, melhore ainda mais a eficiência do tratamento.

Nesse sentido efectuaram-se colheitas em dois anos sucessivos em instalações cujo funcionamento se reputou aceitável, dentro dos parâmetros anteriormente fixados.

Assim na fábrica C efectuaram-se colheitas em Setembro de 1973 e de 1974, colheitas essas que permitiram obter os valores indicados nas Tabelas 10 e 11.

Esta unidade fabril trabalha sem reciclagem de água, sendo o volume de efluentes da ordem dos 9600 m^3 diários, com um BOD_5 próximo dos 350 ppm. Os efluentes são crivados, por meio de um crivo rotativo do tipo já citado, passando em seguida por três tanques. Nos dois primeiros, com uma capacidade total de 5620 m^3, é injectado ar à razão de cerca de 450 m^3/hora. No terceiro tanque, com 3490 m^3 de capacidade, é feita a adição de sulfato de alumínio à entrada (54 g/hora) e de cloro à saída (0,5 ppm).

Na Tabela 10 apresentam-se os valores obtidos em Setembro de 1973 respeitantes:

— ao efluente original;
— ao efluente obtido após crivagem;
— ao efluente à saída do 2.º tanque;
— ao efluente à saída do 3.º tanque.

Tabela 9

Ensaio de depuração biológica efectuada em descontínuo numa bacia de bio-oxidação, com um efluente artificial (concentrado de tomate)

Hora da colheita	Temperatura °C	pH	Sólidos totais	Sólidos solúveis	Sólidos insolúveis	Matéria orgânica	Cinzas	COD	Redução do COD %	
			ppm							
14/5/1974										
18 h	14	6,9	328	327	10	142	186	234	—	← Adição de nutrientes: arejamento
20 h	22	7,4	290	285	5	86	204	238	— 1,7	
22 h	21	7,5	308	286	22	86	222	220	6,0	
15/5/1974										
0 h	20	7,6	274	272	2	96	178	213	9,0	
2 h	20	7,4	268	266	2	84	184	209	10,7	
4 h	19	7,3	244	244	0	60	184	201	14,1	
6 h	20	7,6	240	240	0	56	184	184	21,4	← Adição de sulfato de alumínio
8 h	19	7,4	302	296	6	122	180	190	19,8	
10 h	20	7,4	278	274	4	98	180	184	21,4	
12 h	20	7,8	268	265	3	134	134	137	41,5	
14 h	22	7,8	302	300	2	158	144	108	53,8	
16 h	22	8,0	318	318	0	152	166	97	58,5	

Tabela 10

Valores obtidos em Setembro de 1973 na fábrica C

	Efluente original	Efluente crivado	Efluente arejado	Efluente à entrada no rio	Redução em relação ao efluente original
Temperatura (°C)	28	26	27	19	
pH	7,1	6,1	6,2	6,9	— 0,2 unid.
Sólidos totais	650	412	400	134	— 79 %
Sólidos insolúveis	75	19	17	15	— 80 %
Sólidos solúveis	575	393	383	119	— 79 %
Matéria orgânica	444	232	242	68	— 85 %
Cinzas	206	180	158	66	— 68 %
BOD_5	270	196	140	112	— 59 %
COD	318	231	169	138	— 57 %
BOD_5/COD	0,85	0,85	0,83	0,81	— 0,04

A redução de BOD_5 conseguida foi neste caso de 59 % atingindo um valor que é praticamente idêntico ao do meio de descarga (95 ppm). Daí que a influência seja muito limitada sobre esse mesmo meio, como se comprova pela comparação dos valores observados antes e depois da descarga do efluente. As amostras foram colhidas cerca de 50 m a montante e a jusante do local onde essa descarga é efectuada, obtendo-se os valores seguintes:

	A montante	A jusante
Temperatura	20 °C	19 °C
pH	6,9	6,9
Sólidos totais	120 ppm	102 ppm
Sólidos em suspensão	20 ppm	18 ppm
Sólidos solúveis	100 ppm	84 ppm
Matéria orgânica	42 ppm	36 ppm
Cinzas	58 ppm	66 ppm
BOD_5	95 ppm	102 ppm
COD	102 ppm	121 ppm
BOD_5/COD	0,93	0,84

No ano seguinte foi possível melhorar a exploração do sistema, pela adequação mais perfeita do controle do efluente e da adição de reagentes, obtendo-se os valores transcritos na Tabela 11. A remoção de COD atingiu 88 % obtendo-se um valor inferior ao registado no meio de descarga em colheitas anteriores. Com efeito os valores de COD verificados na ribeira em causa foram respectivamente:

VIII/1071	145 ppm
IX/1971	117 ppm
X/1971	138 ppm
IX/1973	102 ppm

Numa outra unidade fabril, também sem reciclagem da água, adaptou-se contudo um sistema diferente do anterior. Assim as águas tratadas foram exclusivamente as águas poluídas, que após tratamento são diluídas com as águas provenientes da condensação das colunas barométricas. O efluente geral é conduzido, através de uma conduta fechada, até ao curso de água onde é descarregado.

Os efluentes poluídos são tratados de acordo com um esquema análogo ao do sistema descrito. Os dois primeiros tanques têm uma capacidade de 4800 m³ sendo neles injectado ar comprimido à razão de 840 m³/hora. O terceiro tanque com 800 m³ destina-se à coagulação e deposição de sólidos decantáveis, mediante a adição prévia de sulfato de alumínio. À saída das piscinas adiciona-se cloro, sob a forma de hipoclorito de sódio. A crivagem prévia é feita actualmente com um crivo rotativo, tal como no caso anterior. O volume de efluentes tratados é de 5760 m³/dia.

Tabela 11

Valores obtidos em Setembro de 1974 na fábrica C

	Efluente original	Efluente à entrada no rio	Redução em relação ao efluente original
Temperatura (°C)	29	24	— 5 °C
pH	6,5	5,8	— 0,7 unid.
Sólidos totais	565	258	— 54 %
Sól. insolúveis	202	42	— 79 %
Sól. solúveis	363	216	— 40 %
Mat. orgânica	365	118	— 68 %
Cinzas	200	140	— 30 %
Dureza total	25	10	— 60 %
Bicarbonatos	13	17	+ 31 %
COD	562	69	— 88 %

Em relação a este caso dispõe-se de algumas informações que parece importante referir. Inicialmente o sistema era constituído por uma simples crivagem, através de uma grelha, passando por três piscinas, sem qualquer arejamento ou tratamento químico complementar. O volume de armazenagem era de apenas 2800 m^3. Os valores registados ao proceder-se à análise da eficiência deste sistema resumem-se na Tabela 12. Pelos valores aí indicados se conclui que os efluentes «tratados» apresentavam um poder poluente superior ao do efluente original. Isso resultava, por um lado, de um subdimensionamento do sistema e, por outro, da ausência de arejamento. Verificava-se por isso acumulação maciça de resíduos à superfície da água, limitando o rearejamento natural e agravando as condições de anaerobiose.

No ano de 1972 modificou-se o volume das piscinas, pelo aprofundamento das mesmas, instalou-se um crivo (que se revelou aliás não adequado às condições) e iniciou-se o arejamento, recorrendo para tal a alguns pequenos compressores disponíveis. Na Tabela 13 pode verificar-se a melhoria conseguida em relação ao ano anterior, embora a redução do COD fosse apenas de 27 % no mês de Agosto. No mês seguinte a melhoria operada no sistema de crivagem permitiu aumentar a eficiência de tratamento, reduzindo-se o COD de 44% (Tabela 14).

O arejamento continuava a ser o problema mais grave a resolver. A paragem dos compressores por motivos mecânicos permitiu registar o retrocesso da eficiência no decurso de uma colheita efectuada em Agosto de 1973 (Tabela 15).

No mês seguinte a instalação de novos compressores e a adição de nutrientes, tal como fora indicado no respectivo projecto, permitiu estabilizar o sistema e aumentar a sua eficiência que atingiu 75 % (Tabela 16). No mês de Agosto de 1974 novas colheitas confirmaram estes valores e registou-se a redução de 87 % no COD do efluente.

Um aspecto que se verificou ser decisivo para a optimização da exploração do sistema foi a correcção adequada dos teores em N e P do efluente. Nesse sentido se efectuou um ensaio na fábrica C onde se fizeram variar os níveis de nutrientes adicionados, num total de oito ensaios, cada um dos quais se prolongou por um período mínimo de quatro dias. Ao terceiro dia colheram-se amostras de efluente à entrada e à saída do sistema. Os valores obtidos constam das Tabelas 18 e 19. Apesar do carácter preliminar destas observações torna-se patente que:

a) A quantidade de fósforo adicionado parece ser decisiva para a maior ou menor eficiência do sistema.

b) A poluição térmica é muito fortemente reduzida, com as vantagens daí inerentes para a fauna e flora dos cursos de água receptores.

Na campanha de 1975 efectuar-se-ão observações complementares, tendo em conta os ensinamentos colhidos na primeira fase de ensaio.

4.3 — *VALORIZAÇÃO DE RESÍDUOS*

Dentro do combate à poluição, e para além das técnicas destinadas a evitar essa mesma poluição, um outro conjunto de actuações assume, cada dia mais, uma importância maior: a valorização dos resíduos.

Com efeito é bem conhecido o estado de penúria crescente com que a Humanidade se debate no respeitante a matérias-primas. À destruição de substâncias poluentes pode, por isso, opor-se a sua transformação, e consequente produção de substâncias úteis. Nesse sentido se estudou a possibilidade de valorização dos resíduos da indústria do concentrado de tomate. Um subproduto usualmente aproveitado é o repiso dos passadores que,

Tabela 12

Controle da eficiência de um sistema de depuração dos efluentes existente na fábrica D

Características determinadas	Data	Efluente não tratado	Efluente à saída da 1.ª piscina (40 × 20 × 1,5 m)	Efluente à saída da 2.ª piscina (40 × 20 × 1,5 m)	Efluente à saída da 3.ª piscina (40 × 20 × 0,5 m)
Temperatura (°C)	19/VIII	21	22	22	22
	3/IX	28	28	28	28
	25/IX	25	25	25	25
	27/X	26	24	22	21
pH	19/VIII	7,8	7,2	6,8	6,9
	3/IX	6,9	5,9	5,5	5,6
	25/IX	7,0	6,1	6,0	6,2
	27/X	6,8	6,4	5,8	5,9
Sol. totais (ppm)	19/VIII	700	762	652	656
	3/IX	574	616	620	598
	25/IX	590	702	584	528
	27/X	660	576	628	628
Sol. suspensão (ppm)	19/VIII	133	62	9	24
	3/IX	73	29	15	15
	25/IX	218	150	20	32
	27/X	164	24	27	16
Sol. em solução (ppm)	19/VIII	567	700	643	632
	3/IX	501	587	605	583
	25/IX	372	552	564	496
	27/X	496	552	601	612
Matéria orgânica (ppm)	19/VIII	414	412	262	266
	3/IX	402	425	389	403
	25/IX	362	474	444	404
	27/X	532	366	498	412
Cinzas (ppm)	19/VIII	286	350	390	390
	3/IX	172	162	216	180
	25/IX	128	228	140	124
	27/X	128	210	130	216
BOD_5 (ppm)	19/VIII	340	320	276	228
	3/IX	446	1370	847	402
	25/IX	350	3080	880	440
	27/X	380	360	685	480
COD (ppm)	19/VIII	377	350	352	349
	3/IX	504	1785	1094	530
	25/IX	418	3579	1024	526
	27/X	449	427	801	548

Tabela 13

Valores obtidos em Agosto de 1972 na fábrica D

Tipos de efluentes	Temperaturas °C	pH	COD	Sólidos totais	Sólidos solúveis	Sólidos insolúveis	Matéria orgânica	Cinzas
			ppm					
Geral não crivado	25	6,7	364	676	617	59	542	134
Idem, crivado	25	6,5	395	604	550	54	502	102
Água à saída da 3.ª piscina	27	6,6	266	588	560	28	464	124

Tabela 14

Valores obtidos em Setembro de 1972 na fábrica D

Tipos de efluentes	Temperaturas °C	pH	COD	Sólidos totais	Sólidos solúveis	Sólidos insolúveis	Matéria orgânica	Cinzas
			ppm					
Geral, não crivado	26	6,8	359	778	632	146	514	264
Idem, crivado	25	6,9	287	624	574	50	408	216
Água à saída da 3.ª piscina	26	6,3	202	614	601	13	356	258

Tabela 15

Valores obtidos em Agosto de 1973 na fábrica D

Tipos de efluentes	Temperaturas °C	pH	COD	Sólidos totais	Sólidos solúveis	Sólidos insolúveis	Matéria orgânica	Cinzas
			ppm					
Geral, não crivado	33	6,6	526	794	744	50	594	200
Idem, crivado	32	6,6	482	786	722	64	614	172
Entrada na 2.ª piscina	29	5,0	1685	816	807	9	548	268
Entrada na 3.ª piscina	31	5,2	985	794	793	1	570	224
Água à saída da 3.ª piscina	31	5,3	645	894	889	5	670	224

Tabela 16

Valores obtidos em Setembro de 1973 no sistema de depuração da fábrica D

	Efluente original	Efluente à saída das lagoas	Efluente à entrada no rio	Redução em relação ao efluente original
Temperatura (°C)	31	27	27	— 4 °C
pH	6,8	6,4	6,4	— 0,4 unid.
Sólidos totais	892	876	876	— 2 %
Sol. insolúveis	266	18	9	— 97 %
Sol. solúveis	626	858	867	+ 38 %
Matéria orgânica	396	354	358	— 10 %
Cinzas	496	522	518	+ 4 %
BOD_5	604	228	150	— 75 %
COD	671	257	171	— 75 %
BOD_5/COD	0,90	0,89	0,88	— 0,02

uma vez seco, pode ser usado em rações, ou, através de separação da semente, ser usado na obtenção de óleo. Pensou-se, dado o alto teor glucídico do repiso, em preparar, a partir dessa matéria-prima e do efluente, um produto de teor proteico mais elevado, mediante a sua levedurização, isto é, pelo desenvolvimento de leveduras no meio constituído pelo repiso e efluente dos grupos de refinação, seguido de recuperação das substâncias sólidas por centrifugação.

O objectivo procurado é duplo:

a) Valorização do repiso, aumentando o seu teor proteico e em vitaminas do complexo B.

b) Diminuição da carga poluente do efluente dos grupos de refinação.

Realizou-se por isso na fábrica D um ensaio de levedurização recorrendo a um bidão de 200 litros e trabalhando em sistema mais ou menos contínuo. Obteve-se o repiso levedurizado, isto é, uma mistura de repiso + leveduras *(Candida utilis)* com a seguinte composição imediata:

Humidade	7,37 %
Proteína bruta	28,22 %
Gordura bruta	5,60 %
Glúcidos	53,46 %
Celulose	31,07 %
Extr. não azotados	22,39 %
Cinzas	5,35 %

A título comparativo indica-se a composição imediata de repiso não levedurizado:

Humidade	5,9 %
Proteína bruta	10,5 %
Celulose	50,8 %

Como se verifica a melhoria conseguida pela levedurização é muito marcada não só no respeitante ao teor em proteína mas também na diminuição de teor em celulose (devido a um efeito de diluição e à hidrólise da celulose nas condições de pH e temperatura do meio de cultura).

No sentido de determinar quais os quantitativos de azoto e fósforo mais convenientes para a produção de repiso levedurizado procedeu-se a um ensaio factorial 3^2, com duas repetições.

As doses de azoto aplicadas, foram as seguintes:

$N_0 = 0$ g de azoto/litro
$N_1 = 0,5$ g de azoto/litro
$N_2 = 1,0$ g de azoto/litro

O azoto foi fornecido sob a forma de ureia, recorrendo-se ao adubo comercial granulado.

As doses de fósforo aplicadas foram, por sua vez:

$P_0 = 0$ g de fósforo/litro
$P_1 = 0,5$ g de fósforo/litro
$P_2 = 1,0$ g de fósforo/litro

Tabela 17

Valores obtidos em Agosto de 1974 na fábrica D

	Efluente original	Efluente à saída das lagoas	Efluente à entrada no rio	Redução em relação ao efluente original
Temperatura (°C)	23	22,5	30	+ 7 °C
pH	7,2	6,3	7,0	— 0,2 unid.
Sólidos totais	740	700	454	— 39 %
Sol. insolúveis	209	137	68	— 67 %
Sol. solúveis	531	563	386	— 27 %
Matéria orgânica	388	330	118	— 70 %
Cinzas	352	370	326	— 7 %
Dureza total (meq/l)	56	52	48	— 14 %
Bicarbonatos (mg/l)	38	37	28	— 26 %
COD	697	382	88	— 87 %

O fósforo foi adicionado sob a forma de adubo superfosfato de cal a 18 %.

O produto obtido foi analisado, determinando-se o teor em azoto, pelo método de Kjeldahl, e em fósforo, pelo método molibdato-vanadato.

Os teores em azoto, expressos em relação à matéria seca, determinados nas várias amostras foram os seguintes:

	P_0	P_1	P_2
N_0	3,86 %	3,38 %	3,32 %
N_1	5,00 %	5,06 %	4,73 %
N_2	6,36 %	5,72 %	5,86 %

A análise de variância dos resultados obtidos conduziu aos seguintes resultados:

Causas de variação	G. l.	S. dos Q.	Q. m.	F	
Blocos	1	0,0440	0,0440	1,09	N. S.
Tratamentos	8	19,2060	2,4008	59,43	* *
N	2	18,2820	9,1410	226,26	* *
P	2	0,6431	0,3216	7,96	
N × P	4	0,2809	0,0702	1,74	
Erro	8	0,3229	0,0404	—	
Total	17	19,5729	—	—	

O desvio padrão é portanto de ± 0,20 %. A menor diferença significativa entre tratamentos é, portanto, de ± 0,42 %. Considerando, por outro lado, as médias segundo os níveis de azoto aplicados concluiu-se serem

N_0 3,52 %
N_1 4,93 %
N_2 5,98 %

Como a menor diferença significativa entre essas médias seria igual a ± 0,24 %, concluiu-se serem significativamente diferentes todas elas, aumentando o teor em azoto do produto levedurizado com o aumento de quantitativo de ureia adicionada.

Quanto às médias segundo os níveis de fósforo adicionados, são respectivamente:

P_0 5,07 %
P_1 4,72 %
P_2 4,63 %

Sendo a menor diferença significativa também igual a ± 0,24 % regista-se a evolução negativa do teor em azoto do produto levedurizado, embora não haja significância na diferença entre P_1 e P_2. Do ponto de vista prático pode concluir-se ser suficiente o quantitativo de fósforo do substracto, não sendo necessário adicionar este nutriente no que se refere ao valor proteico do produto obtido.

Quanto aos teores em fósforo, expressos em relação à matéria seca, os valores determinados foram os seguintes:

	P_0	P_1	P_2
N_0	0,52 %	1,75 %	2,29 %
N_1	0,56 %	1,51 %	2,31 %
N_2	0,51 %	1,85 %	2,31 %

A análise de variância conduziu aos valores seguintes:

Causas de variação	G. l.	S. dos Q.	Q. m.	F	
Blocos	1	0,0109	0,0109	0,22	
Tratamentos	8	22,5312	2,8164	57,64	* *
N	2	0,0582	0,0291	0,60	
P	2	22,2479	11,1240	227,68	* *
N × P	4	0,2251	0,0563	1,15	
Erro	8	0,3909	0,0489	—	
Total	17	22,9330	—	—	

O desvio padrão é portanto de ± 0,22 %, sendo igual a ± 0,47 % a menor diferença significativa entre tratamentos. As médias por níveis de azoto adicionado são iguais respectivamente a:

N_0	1,51 %
N_1	1,46 %
N_2	1,55 %

Não há diferenças significativas entre estes valores dado que o nível de significância corresponde a uma diferença de ± 0,27 %.

Quanto às médias segundo os níveis de fósforo adicionado ao substracto elas são iguais, respectivamente, a:

P_0	0,53 %
P_1	1,69 %
P_2	2,30 %

Como a menor diferença significativa entre médias é de ± 0,27 % conclui-se aumentar o teor em fósforo do produto levedurizado com o nível deste nutriente adicionado ao meio de cultura. De acordo com os fins pretendidos poderá ou não justificar-se a adição de fósforo. A opção dependerá igualmente

Tabela 18

Valores obtidos num ensaio de funcionamento com diferentes níveis de nutrientes adicionados

Data da colheita	12/9/1974			19/9/1974			21/9/1974			24/9/1974		
Tomate laborado em 24 h (t)	520			394			493			239		
% de granel	57,6			56,8			58,4			54,3		
N:	40 kg			30 kg			50 kg			30 kg		
P_2O_5:	10 kg			10 kg			15 kg			15 kg		
	A	B	Redução em %	A	B	Redução em %	A	B	Redução em %	A	B	Redução em %
Temperatura (°C)	31	26	— 16	31	24	— 23	29	24	— 17	24	20	— 17
pH	6,8	6,9	+ 1	6,6	6,1	— 8	6,5	6,8	+ 5	6,8	6,3	— 7
Sólidos totais (ppm)	508	368	— 28	722	394	— 45	565	258	— 54	465	408	— 12
Sol. insolúveis (ppm)	80	15	— 81	134	8	— 94	202	42	— 79	77	64	— 17
Sol. solúveis (ppm)	428	353	— 18	588	386	— 34	363	216	— 40	388	344	— 11
Mat. orgânica (ppm)	316	202	— 36	526	236	— 55	365	118	— 68	295	251	— 15
Cinzas (ppm)	192	166	— 14	196	158	— 19	200	140	— 30	170	157	— 8
Dureza total (meq/l)	28	24	— 14	33	26	— 21	25	10	— 60	40	28	— 30
Bicarbonatos (mg/l)	14	23	+ 64	10	21	+ 110	13	17	+ 31	18	26	+ 44
COD (ppm)	206	87	— 58	310	156	— 50	562	69	— 88	360	170	— 53

Tabela 19

Valores obtidos num ensaio de funcionamento com diferentes níveis de nutrientes adicionados

Data da colheita	27/9/1974			30/9/1974			4/10/1974			7/10/1974		
Tomate laborado em 24 h (t)	562			438			595			268		
% de granel	63,4			63,2			60,1			0		
N:	40 kg			30 kg			30 kg			40 kg		
P_2O_5:	15 kg			10 kg			15 kg			10 kg		
	A	B	Redução em %	A	B	Redução em %	A	B	Redução em %	A	B	Redução em %
Temperatura (°C)	31	24	— 23	28	18	— 36	31	23	— 26	31	25	— 19
pH	6,9	6,0	— 13	6,6	6,6	0	6,5	5,8	— 15	6,1	6,1	0
Sólidos totais (ppm)	457	329	— 28	658	590	— 10	567	340	— 40	490	369	— 25
Sól. insolúveis (ppm)	83	42	— 49	94	15	— 84	70	27	— 61	120	24	— 80
Sól. solúveis (ppm)	374	287	— 23	564	575	+ 2	497	313	— 37	370	345	— 7
Mat. orgânica (ppm)	324	209	— 35	472	450	— 5	401	294	— 27	362	267	— 26
Cinzas (ppm)	133	120	— 10	196	140	— 29	166	146	— 12	128	102	— 20
Dureza total (meq/l)	31	18	— 42	58	14	— 76	21	18	— 14	22	14	— 36
Bicarbonatos (mg/l)	18	20	+ 11	15	22	+ 47	11	20	+ 82	9	17	+ 89
COD (ppm)	584	205	— 65	686	170	— 75	685	146	— 79	335	102	— 70

do teor em cálcio, de modo a evitar-se o desequilíbrio de relação Ca/P.

A possibilidade de valorização dos resíduos do fabrico de concentrado de tomate por esta via está, portanto, amplamente demonstrada. A opção concreta dependerá, contudo, dos aspectos económicos do problema. É necessário atingir uma dimensão mínima para que esta solução seja economicamente viável, uma vez que existe uma outra solução: a secagem do repiso e o tratamento dos efluentes. Numa óptica de conservação bio-energética e de optimização da utilização de recursos, a valorização é sem dúvida preferível. A prazo mais ou menos curto a necessidade de aproveitar todos os recursos disponíveis conduzirá, obrigatoriamente, disso estamos certos, a soluções deste tipo para todas as indústrias alimentares.

5 — RECIRCULAÇÃO DOS EFLUENTES TRATADOS

A indústria do concentrado de tomate implica um consumo muito grande de água, desde que não se recorra a técnicas de recirculação. Este facto, aliado à fácil biodegradabilidade das substâncias poluentes, levou a considerar-se a possibilidade de, mediante um tratamento mais intenso, se conseguir reduzir o nível de poluição dos efluentes a valores que permitam a sua reutilização.

O sistema instalado numa fábrica em 1974, consistia nas seguintes fases processuais:

a) Crivagem num tamizador rotativo.

b) Passagem através de duas piscinas arejadas, com a capacidade total de 2400 m³ e nas quais o efluente é injectado com 600 m³/hora de ar, ou seja, 180 kg de oxigénio/hora.

c) Passagem através de uma bacia de decantação com 1200 m³, com adição de sulfato de alumínio e leite de cal para eventual reajustamento do pH e também do cloro, sob a forma de hipoclorito de sódio.

d) Passagem através de um sistema tradicional de tratamento de águas com dois decantadores de 288 m³ de capacidade cada um, filtração através de filtro de areia e clorinação, com cloro gasoso.

De início adicionou-se azoto e fósforo mas cedo se interrompeu uma vez que, dada a situação em circuito fechado, se geraram condições propícias ao desenvolvimento de algas (controladas imediatamente recorrendo à cânfora).

O sistema não funcionou em sistema fechado em

Tabela 20

Valores do COD ao longo do sistema de depuração (funcionando em circuito fechado)

Colheita	Efluente não tratado	À saída da bacia de decantação	No final do tratamento
1	476	508	93
2	760	664	—
3	948	787	137
4	1028	552	—

sentido absoluto, uma vez que se tornou necessário repor as perdas por evaporação e adicionar água limpa. De qualquer modo conseguiu-se reduzir o consumo, que seria em condições usuais de 500 000 m^3, para cerca de 30 000 m^3.

Na Tabela 20 apresentam-se os valores do COD registados em diversos pontos do circuito, em alturas diferentes. A eficiência é, como se pode ver, elevada. Por outro lado, há que referir a má qualidade da água de alimentação cujos valores de COD registados em 5 amostras variaram entre 69 ppm e 113 ppm, com um valor médio de 96 ppm.

Como é evidente, o sistema para funcionar correctamente implica um consumo elevado de reagentes, nomeadamente sulfato de alumínio e cloro. O significado de que se reveste, porém, em termos de instalação de indústrias alimentares deste tipo em zonas com reduzidas disponibilidades hídricas, e em termos de redução de poluição são bem evidentes.

Há que adoptar corajosamente e de forma coerente as soluções compatíveis com o modelo de desenvolvimento adoptado para a sociedade em que se vive. O desenvolvimento erigido em objectivo é incompatível com uma qualidade de vida elevada. Um naturalismo romântico é igualmente inadmissível com uma prosperidade generalizada. Entre os dois extremos a adopção criteriosa de medidas adequadas pode conduzir ao objectivo pretendido: uma sociedade próspera vivendo num ambiente equilibrado. Esse objectivo é possível. Depende de todos nós torná-lo uma realidade.

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SUMMARY

The industries of tomato concentrate, of large economical significance in Portugal are also an important pollutant of Portuguese rivers and lakes. Data collected for three years in different industrial plants are presented with the objectif of identifying the causes for the pollution and discusses the results obtained through a biological treatment (accelerated bioxidation followed by a complementary chemical treatment). Data concerning the development of by-products and effluent recycling are also given.

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OPERATING COST ANALYSIS AND ESTIMATION IN THE CHEMICAL PROCESS INDUSTRIES (1)

Economic justification is usually the most important factor when considering the future of a project. It is therefore important that cost estimates are as accurate and reliable as possible. Cost estimation is traditionally split into capital or fixed costs and operating or variable costs. The latter may be subdivided in several ways and examples from a range of industries are included. This enables the most significant operating cost areas to be identified and related to traditional operating cost estimation techniques. Rapid and overall techniques are developed from this treatment and compared to recent developments in this area.

1 — INTRODUCTION

There are probably as many different ways of analysing manufacturing costs as there companies engaged in this task. The subject of this paper is to examine how individual costs are built up to a total manufacturing or product cost, which with mark-up gives a sales price. It will be seen that many of the individual costs are insignificant, and certain items assume major importance. This analysis is useful both for identifying cost sensitive areas and also for cost estimation. More detailed analysis is useful for budgeting, price control and management accounting, optimisation of existing product evaluation, and new project evaluation, none of which are discussed at length. The total manufacturing cost, total product cost, or total cost may typically be broken down as shown below in fig. 1, which is detailed further in fig. 2.

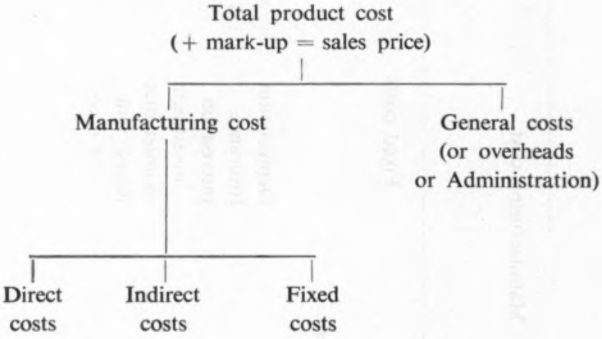

Fig. 1
Typical generalised breakdown of costs

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(1) Presented at CHEMPOR' 75 held in Lisbon, 7-12 September 1975 at the Calouste Gulbenkian Foundation Center.
Papers presented at this International Chemical Engineering Conference can be purchased directly from Revista Portuguesa de Química (Instituto Superior Técnico, Lisboa 1, Portugal) at the following prices per volume sent by surface mail, postage included (in Portuguese Escudos):

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This paper was presented at the Management studies section.

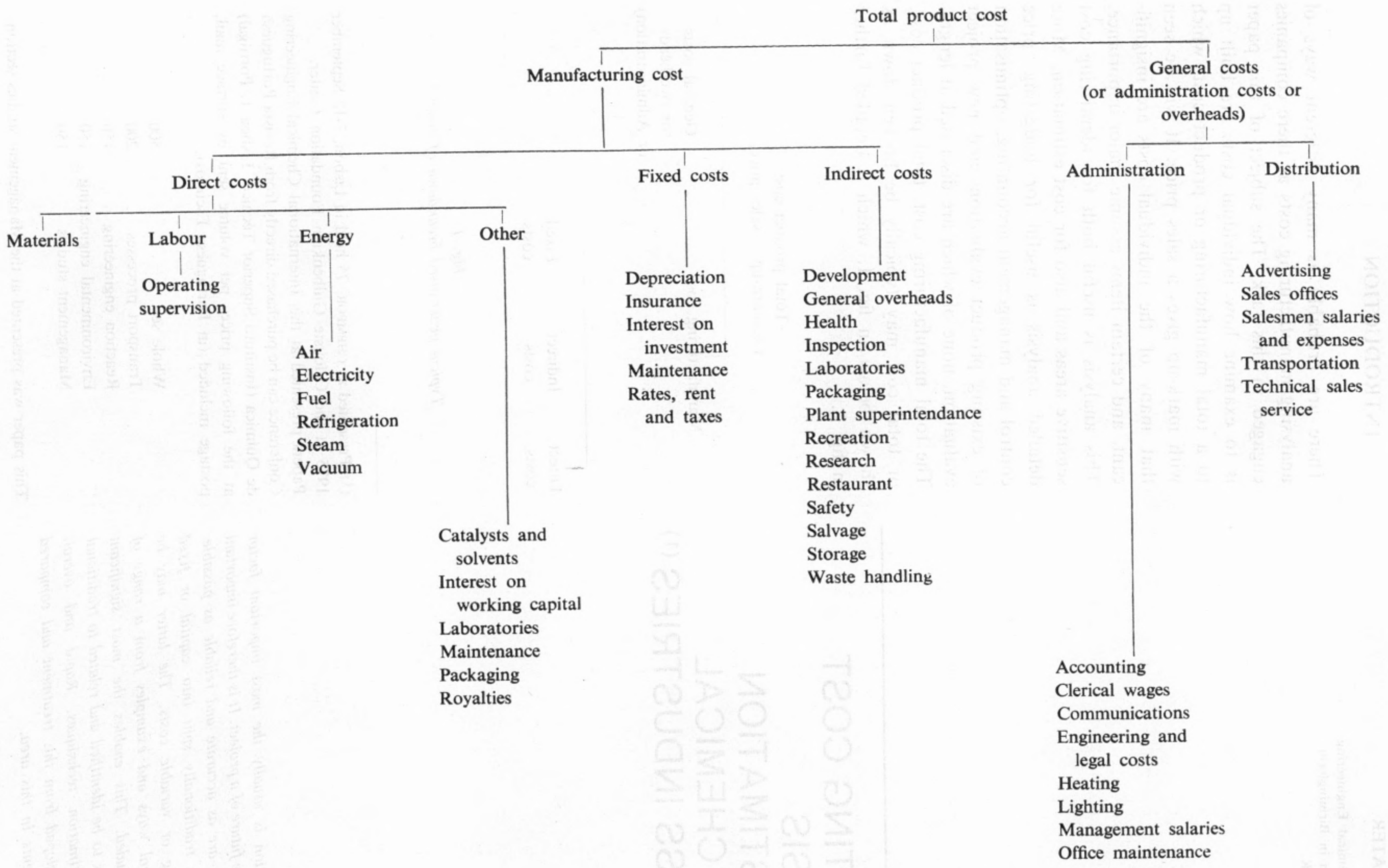

Fig. 2
Typical breakdown of product cost

Fig. 1 shows a typical generalised breakdown of costs which is often helpful in production costing and accounting. For cost estimation and analysis, the chemical engineer is not usually interested in such detail, only in broad headings which encompass many of the minor items shown.

2 — COST ANALYSIS

2.1 — *CASE STUDIES*

In order to provide realistic figures for the breakdown of costs, actual costs are shown below as Table 1 including a typical analysis. This demonstrates some of the problems encountered in collating cost data for analysis and indicates significant cost areas.

Several classifications of operating cost may be deduced from examples such as these:

1) (Raw) materials
   Labour
   Energy or power or utilities
   Administration and/or overheads and/or distribution
   Depreciation and related fixed costs
2) Direct, production or variable costs
   Indirect costs
   Fixed costs
3) Variable (operating) costs
   Fixed (capital) costs

Production cost estimation is usually based initially on one of the above classifications or some variation, thereof, and cost data is usually available in a similar form. The interrelationships of the classifications may be shown in a matrix of management functions versus costs which is shown in fig. 3. This indicates the complexity of a cost analysis exercise and the problems likely to be encountered in deriving a realistic estimation technique.

The simplest classification of costs into variable and fixed is frequently adopted. Variable costs tend to vary directly with volume of output and while linear relationships are usually assumed which gives the well-known straight line breakeven chart, this is probably only true for small changes in output and is not applicable for substantial changes. For example raw materials prices could change in bulk discounts for significant changes in output. There are other items that have both a fixed and variable element and either form a third category of indirect (or semivariable) costs, or may be arbitrarily assigned to either the variable or fixed cost classification. Fixed costs remain a distinct category and tend to be unaffected by variations in output.

	Production costs	Selling costs	Distribution costs	Administration	Research development
Raw materials	+				
Fuel	+			+	+
Energy	+			+	+
Labour					
— operating	+		+		+
— supervisory	+		+		+
— clerical		+	+	+	
— managerial		+	+	+	+
— selling		+			
— technical	+	+	+		+
Buildings	+	+	+	+	+
Plant	+		+		+
Land	+	+	+	+	+

Fig. 3
Management functions versus costs

Table 1

Typical analysis

	Percentage of total cost		
Raw materials	31		
Labour	11		
Supervision	2		
Maintenance	2		
Plant supplies	1		
Royalties and patents	2		
Utilities	8		
Direct manufacturing cost		57	
Payroll overhead	2		
Laboratory	2		
Plant overhead	9		
Packaging	1		
Shipping	1		
Indirect manufacturing cost		15	
Depreciation	4		
Property taxes	1		
Insurance	1		
Fixed manufacturing cost		6	
Manufacturing cost			78
Administration	4		
Sales	11		
Research	5		
Finance	2		
General expenses			22
Total cost			100

Air Separation [2]

	% of total cost
Utilities	25
Chemicals	2
Labour	14
Maintenance	6
Plant overheads	12
Fixed charges	41
	100

Gas [1] *1968-9*

	% of total cost
Feedstock (net cost)	26
Labour	27
Other materials	17
Rates and Gas Council	4
Capital charges and provision for for surplus (gross return)	26
	190

Table 1 (cont.)

Sulphuric acid [3] *1964/5*

	% of total cost			
	250 tons/day from sulphur		200 tons/day from pyrite	200 tons/day fron anhydrite
Raw materials	70		50	18.4
Electrical power	2.5			
Process and boiler water	0.5			
Cooling water	0.5	Conversion		
Labour and supervision	6	costs	23.4	40.2
Maintenance and sundries	9			
Depreciation	11.5	and interest	26.6	41 4
(Steam credit)	(18.7)			
(Calcine credit)			(3.2)	
(Cement credit)				(20.6)
	100		100	100

Acrylonitrile [4] *1966/7*

	% of total raw material cost	% of total cost
Propylene	63.1	
Ammonia	26.3	
Catalyst & Chemicals	10.6	
	100	
Byproduct credit:		
Hydrogen cyanide	15.0	
Acetonitrile	69.5	
Net raw material cost	15.5	20.6
Steam		11.2
Power		5.6
Water		2.8
Labour and supervision		5.6
Overheads		8.4
Maintenance		15.3
Depreciation		30.5
		100

Table 1 (cont.)

Cement [21] *1966-1969*

	% of selling price			
	1966		1969	
Raw materials	4.6		5.3	
Wages	10.5		11.4	
Maintenance	7.7		8.3	
Fuel	16.3		15.8	
Power (electricity)	7.0		7.8	
Works overheads	5.4		6.2	
General administration	3.5		3.9	
Depreciation	4.7		5.5	
Others	1.3		1.3	
Manufacturing cost		61.0		65.5
Delivery	16.2		17.0	
Sales	6.4		6.4	
Margins and discounts	5.5		5.5	
Total cost		89.1		94.4
Profit	10.9		5.6	
		100		100

(Average for the industry)

This rough division into variable and fixed costs is helpful for preliminary analysis of existing processes in early stages of economic analysis. However it does little to help identify cost sensitive areas or to assist in establishing cost estimation procedures. The more detailed breakdown of variable costs into raw materials, labour, energy, and overheads is a considerably more understandable and realistic way of estimating product costs and has long been accepted by chemical engineers. There is therefore a considerable amount of data and documentation available, although the former tends to be very elusive.

2.2 — *MATERIALS*

The most significant cost element for most products in the chemical process industries is for materials. This has generally been found to range between 10 % and 90 % of the total cost of production. Grumer [5] analysed the production costs of 30 organic chemicals and found that the raw material element ranged from 8 % to 93 % of the product price, with a crude average of just over 50 %. Examination of the figures suggested that there may be two broad classes of product: chemical intermediates from basic hydrocarbon raw materials which contribute roughly 35 % to the product price; and organic intermediates of a more complex nature often involving oxidation or inorganic acids, when raw materials contribute roughly 75 % to the product price. There are other references to the high proportion of raw material costs in overall production costs, for example Peters and Timmerhaus [6] quote 10-50 % and Aries and Newton [7] 30-70 %.

2.3 — *LABOUR*

Either total labour or direct operating labour is usually quoted. The latter is invariably the basis for calculating other costs such as supervision and overheads, and this is discussed later. A brief examination of the contribution of direct labour costs to selling price is given in Table 2 which indicates that they often do not exceed 5 % of the selling price. ARIES and NEWTON [7] however suggest that labour constitutes 5-10 % of the manufacturing expense for large scale fluid processes, and from 15-25 % in operations requiring considerable handling (*e.g.* solids).

Table 2

Contribution of direct labour costs and energy costs to selling price

Chemical	1972 selling price (s. p.) U.S.$/ton [9]	Labour cost U.S.$/ton [10]	% of selling price	Energy cost U.S.$/ton [10]	% of selling price
Acetaldehyde	198	6.36	3.2	4.45	2.2
				2.31	1.2
				7.11	3.6
Acetone	129	5.76	4.5	21.90	17.0
				10.37	8.0
Acrylonitrile	286	6.85	2.4	43.31	15.1
		7.25	2.5	19.70	6.9
		6.25	2.2	19.70	6.9
Ammonium sulphate	27.5	2.62	9.5	0.55	2.0
Aniline	330			5.60	1.7
Benzene	68.5	0.62	0.9	2.17	3.2
		0.62	0.9	1.66	2.4
				2.13	3.1
				2.40	3.5
				2.34	3.4
				6.91	10.0
				2.30	3.4
				4.73	6.9
Carbon tetrachloride	248	7.46	3.0	1.05	0.4
Chlorine	82.5	1.21	1.5	18.39	22.3
		1.21	1.5	20.41	24.8
		1.21	1.5	20.44	24.8
Cyclohexanone	396	0.22	0.06	19.27	4.9
Ethylene oxide	297	0.39	0.13	13.00	4.4
Isopropanol	165			11.22	6.7
Per/Trichlorethylene	220			18.0	8.2

N. B. — These figures are for illustration only, as the age of the data is not taken into account, and the selling prices are current. This effect was properly considered in developing the equation quoted in the text.

2.4 — *ENERGY*

Little has been published on the significance of energy costs to total manufacturing cost. PETERS and TIMMERHAUS [6] suggest that energy costs are 10-20 % of the selling price of a chemical. Alternatives quote a fixed allowance for energy of 0. 3 to 0. 5p per lb., or allow 10 % of raw material cost or deny that the contribution to overall costs is significant. A brief survery of a number of chemicals in Table 2 shows that energy costs appear to contribute between 1 % and 25 % of the selling price of a chemical.

2.5 — *OTHER COSTS*

This is perhaps the least well defined area, and one that is most difficult to quantify. For overheads and distribution, a typical overall figure seems to be around 15 % of sales price for most chemicals apart from pharmaceuticals when it becomes about 40 % [8]. Figures for administration, research and selling as percentages ot selling price are quoted under the analogous heading of cost estimation.

3 — COST ESTIMATION

The same pattern to that derived above by analysis of operating costs is followed for surveying available estimating methods.

3.1 — *MATERIALS COSTS*

Having established the importance of materials costs, how are these estimated? Costs of many chemicals are published regularly in a variety of journals such as «European Chemical News» and «Chemical Marketing Reporter» (formerly «Oil Paint and Drug Reporter»). Listed prices are invariably related to particular quantities, and occasionally qualities also, and these must be considered in terms of the likely requirements of the project. Tanker quantity prices for several gallons a week are as erroneous as laboratory reagent prices for 500 tons per week. It is well known that there is a relationship between price and quantity and the precise nature often deserves investigation.

Of particular difficulty in establishing costs are primary fuel materials, considered here as chemical feedstocks. Coal for example is location sensitive, and is not only considerably cheaper at the pit head than away from it but also the price can vary according to the location of the pit head. This may not only be due to the transportation and handling costs, but may be influenced by policy, political or social factors. Crude petroleum fractions such as naphtha often depend on special «deals» for their prices. There are also those heavy organics such as ethylene that are expensive to transport in small quantities and are usually sold «over the fence» and often to a captive market. Some idea of minimum likely costs of primary fuel materials may be obtained from industrial and government publications such as «Prices and Incomes Board», or by comparison and/or analogy. Some prices for fuels are given in Table 3. Much depends on the size of plant to be built and the raw material requirements and availabilities, and the number of alternatives then increases considerably.

3.2 — *MATERIALS PRICE — QUANTITY RELATIONSHIP*

The prices of feedstocks and products tend to follow a similar pattern of fall in price or cost with increased quantity of material produced or used. This is important to consider when planning the size of a project and its longer-range prospects. Several studies [e. g. 11-13] have given rise to an appropriate correlation known as the «minus four tenths» rule or «minus one third» rule.

$P = KQ^a$ where

P = price; money units per unit

Q = annual units produced

a = constant = -0.4 or sometimes -0.33.

Table 3

Typical fuel feedstock prices (1975)

Fuel oil	Basic zone price p/gal	 £/ton	Cost/therm p
3500 sec grade	19.3	44.7	10.9
950 sec grade	19.7	45.6	11.2
200 sec grade	21.0	48.6	12.1
35 sec grade	23.9	55.3	14.5

The price is subject to bulk discounts of up to 20 % according to quantity and supply situation.

Industrial coal	Delivered price £/ton	Cost/therm p
Beans	20.00	7.40
Smalls	17.00	7.00

Natural gas	Average price £/ton	Cost/therm p
Interruptible load	42.7	8.5
Uninterruptible load	64.1	12.0

L. P. G.	Delivered price £/ton	Cost/therm p
U. K., industrial	52	11.0-12.0
Europe, propane	70	14.80
butane	60	12.40

Electricity

Subject to wide variation depending on season, time of day, peak load, and size of load. For large industrial loads a reasonable figure is 1.6 p/kWh which is equivalent to 46.9 p/therm.

Table 4

Cost of services (1975)

Electricity	1.6 p/kWh	(see also Table 3)
Gas	85-120 p/1000 SCF	(see also Table 3)
Oil	19-24 p/gal	(see also Table 3)
Coal	£17-20/ton	(see also Table 3)
Steam	£5-6/ton or £2.0-2.5/1000 lb.	
Cooling water	20-40 p/1000 gals or 5.9 p/m^3	
Process water	40-60 p/1000 gals or 9-13 p/m^3	
Compressed air	2-4 p/1000 SCF	

It is possible to relate these exponents to the familiar «two thirds» or «six tenths» rules concerning concerning economy of scale:

$$\frac{I_1}{I_2} = \left(\frac{Q_1}{Q_2}\right)^b$$

where I = capital investment
b = a constant = 0.6 or 0.66

3.3 — *LABOUR*

The traditional method of assigning a certain number of men to specified items of equipment [7,14] is considered to be becoming outdated with the advent of sophisticated control systems and on-line computer control.

The alternative to this approach which accumulates with experience, are correlations such as Wessel [15] proposed for labour requirements which may be expressed as an equation:

$L = KNQ^{-0.76}$ where
L = Operating labour, man hours per ton of product.
N = Number of process steps. These are analogous and similar to Functional Units which have been adequately described elsewhere.
Q = Plant capacity, tons per day.
K = Constant = 23 for batch operations.
= 17 for operations with average labour requirements
= 10 for well instrumented continuous process operations

There are other techniques of direct labour cost estimation based on a time study approach and also based on simulation of plant or as a nomograph. There has been general agreement on Wessels estimating technique (with few exceptions [11]) which has been invariably adopted in one form or another and is recommended by most major texts.

The relationship between operating labour costs and plant capacity and number of functional units or process steps has been further investigated by Fidgett [10]. A number of models were examined [16] and the most successful was:

$L = 5.849.N.Q^{-0.867}$ where
L = Labour cost, U.S. dollars per ton product
N = Number of functional units
Q = Plant capacity thousand tons per year
I = Adjusted capital cost of plant, $\dfrac{\text{thousand dollars}}{\text{ENR index,}}$
base 100 in 1913
1972 basis

This includes a greater effect of scale than appeared when Wessel derived his correlation. The result is thought to support Wessel's idea of different categories or process, and that the labour costs are likely to fall within a broad band with no clear classifications but defined by constants of 2.6 and 12.5. There is clearly room for improvement in defining terms and improving the correlation. Labour costs vary with time and there are a number of widely published indices in both the technical press and government publications.

In order to compare Wessel's and Fidgett's correlation, it is assumed that there are 330 days in a year, that labour costs £2 per hour for U.K. conditions or $6 per hour for U.S.A. conditions (including social service contribution, pensions, etc.) and using Wessel's coefficient for well instrumented continuous operations; Wessel's correlation then becomes:

$L = £1{,}800.N.Q^{-0.76}$ or $\$5{,}400.N.Q^{-0.76}$ where
L = direct labour costs per ton product, £ or $
N = number of process steps
Q = plant capacity, long or metric tons per year
£ for U.K. and European plants
$ for North-American plants.

This may be re-written as an annual direct labour cost (Lt):

$Lt = £1{,}800.N.Q^{-0.24}$ or $\$5{,}400.N.Q^{-0.24}$

and Fidgett's analogous correlations become

$L = £1{,}030.N.Q.^{-0.867}$ or $\$3{,}100.N.Q^{-0.867}$ and
$Lt = £1{,}030.N.Q^{0.133}$ or $\$3{,}100.N.Q^{0.133}$

Other labour expenses are very difficult to identify and quantify as they appear under such a wide diversity of headings. Labour related costs are commonly 10 % of the direct labour; supervision is usually a fixed percentage of operating labour and often set at 25 %; administration and sales «labour» and management are usually contained in a blanket figure for overheads, administration and distribution. A quoted figure [17] for this last item is 1.28 times the direct labour costs. Alternatively a figure for administration overheads excluding capital charges is given as 14 % of the selling price [11]. This is also discussed later.

3.4 — *ENERGY*

Otherwise known as power and fuel or utilities, this is the third significant cost area that may be well defined in a chemical plant. Included here are steam, electricity, water, air, fuel, gas, oil, refrigeration, etc. Typical values are given in Table 4. These figures are generally and currently applicable to the U.K. Variation in costs may occur due to a number of factors including location, scale of operation, political pressures, and relative economics of buying in energy or providing some in-plant utilities.

Typical fuel prices for the U.K. are outlined in Table 3 [18]. It should be noted that prices have approximately trebled over the last four years [16] after a relatively long period of stability, and under these circumstances therefore future predictions are difficult.

To date no alternative to a relatively detailed energy requirement estimate has been found. However, FIDGETT [10] has also analysed the energy costs of a wide variety of processes and obtained the following equation [16]:

$$E = 0.748 \left(\frac{I}{Q} \right)^{0.751} N^{0.774} \qquad \text{where}$$

E = energy cost, dollars per ton of product

Q = plant capacity, thousand tons per year

I = adjusted capital cost, $\dfrac{\text{thousand dollars}}{\text{ENR index,}}$ base 100 in 1913

N = number of functional units

1972 basis

As the energy cost given by this correlation is a function of investment, both of these will increase with time which will tend to give an approximation that is independant of time. The recent energy and other problems however make such an assumption much less credible in the short term although it is anticipated that this effect will disappear as price changes work their way through and costs generally become stabilised.

This should be treated with great caution. It might be thought surprising that such a correlation was obtained between energy cost and these basic process parameters, and that inclusion of other, more relevant parameters such as a thermodynamic function, could improve the correlation. There is clearly much scope for further investigation, not only into alternative models and parameters, but also into the continued problem of data collection and reliability in deriving a correlation.

3.5 — *OTHER COSTS*

The remainder of costs may be divided into administration distribution research and indirect costs; and fixed costs — capital investment, depreciation and related costs which are considered later. The former group are almost impossible to quantify and are often lumped together as «overheads» (which may or may not include distribution). Perhaps one of the major difficulties is delineating what should or should not be included, and a variety of methods have been suggested for estimating these costs.

HAPPEL [19] quotes a figure of 125 % of direct labour costs plus 11 % per year of plant investment for all costs other than materials, energy and direct labour. Both ARIES and NEWTON [7], PETERS and TIMMERHAUS [6] and HOLLAND [21] add a percentage of various basic parameters such as direct labour costs for a number of items in this category, but leave others for more detailed analysis and costing. HACKNEY [20] provided an analysis of sales, management, research and administration costs for a range of products which is summarised in Table 5. This is probably one of the more useful approaches to cost estimation in this area.

Table 5

Administration, sales and research costs [20]

	Administration costs (% of sales price)
All products	4.0

	Research costs (% of sales price)
Old chemical, old process	1.5
Old chemical, new process	
— conventional	3.0
— radical	5.0
New chemical, new process	
— conventional	3.5
— radical	5.5

	Selling costs (including technical service) (% of sales price)
Old line product	
— contract sales	2.0
— non contract sales	8.5
Speciality product	
— old product	11.0
— new product	16.0
Completely new product	23.0

	Overall cost (% of sales price)	
	Lowest conditions	Highest conditions
Administration	4.0	4.0
Research	1.5	5.5
Selling	2.0	23.0
TOTAL	7.5	32.5

3.6 — *FIXED COSTS*

Examination of the profitability of a process is best carried out using a discounting technique to include the time value of money, such as Net Present Worth or Discounted Cash Flow Rate of Return. In these methods the capital investment and some related costs such as working capital are included at the time of expenditure rather than being spread over the life of the project. The custom of counting depreciation as a fixed annual cost is valuable for a number of reasons including accounting purposes, portraying a realistic picture of the decreasing value of the original assets, and optimising or maximising tax relief. In other words depreciation figures are essentially book transactions and have little meaning in real terms. There are a wide variety of techniques for calculating depreciation mainly of interest to accountants (in [22] for example). The most common is straight line depreciation over the life of the project, which is often taken as ten years in the chemical process industries as a first estimate. Investment related costs include maintainance and working capital. There seems to be general agreement on maintenance costs as follows

	% on capital investment
Low utilisation and/or simple equipment	2-4
Average usage and conditions	5-6
High usage and/or severe conditions and/or complex operations	7-12

There are a number of less known alternatives which include correlations with electricity consumption [23], and assembling an overall maintenance cost from examination of individual plant item requirements [7]. Working capital includes stocks of raw and other materials and is usually taken as 15 % of capital investment although alternatives have been suggested such as 30 % of annual sales, and a composite figure of inventory costs for raw materials, semifinished materials, and finished material for one month [24].

4 — RAPID METHODS OF ESTIMATING OPERATING COSTS

There are few published methods for rapid estimation of operating costs, but it is not difficult to derive correlations from information provided in the literature. This invariably follows the same pattern laid out for cost analysis and estimation by summing the cost of materials, labour and related costs, energy and fixed investment related costs. These are invariably derived and discussed below, and compared in Table 6. The following notation is used throughout this section:

R = (Raw) materials
L = Direct operating labour
E = Energy (or power or utilities)
I = Fixed investment
S = Selling price of product

Peters and Timmerhaus [6]

a)	Raw materials	R				
b)	Labour		L			
c)	Supervision, 15 % L		0.15L			
d)	Utilities			E		
e)	Maintenance, 2-20 % I				0.06I	
f)	Operating supplies, 15 % e				0.009I	
g)	Laboratories, 10-20 %I		0.15L			
h)	Royalties 2-6 % S					0.04S
j)	Catalysts and solvents					
k)	Property taxes, 1-4 % I				0.023I	
l)	Insurance				0.01I	
m)	Rent, 8-10 % rented property					
n)	Plant overheads, 50-70 % b + c + e		0.69L		0.036I	
o)	Administration, 40-60 % L		0.5L			
p)	Distribution and marketing 2 — 20 %S					0.05S
q)	Research and development, 2-5 % S					0.035S

Total operating cost = R + 2.49L + E + 0.138I + 0.125S
(excluding depreciation and interest)
= 1.14R + 2.85L + 1.14E + 0.158I

Aries and Newton [7]

a) Raw materials	R			
Direct labour	L			
Supervision, 10-25 % L	0.18L			
Maintenance, 2-10 % I			0.065I	
Plant supplies, 15 % maintenance			0.01I	
Royalties 1-5 % S				0.03S
Utilities		E		
Payroll overhead, 15-20 % L	0.18L			
Laboratory, 10-20 % L	0.15L			
Plant overhead, 50-100 % L	0.75L			
Packaging, up to 40 % S				—
Freight				
Property taxes, 1-2 % I			0.015I	
Insurance			0.01I	

Total operating cost = R + 2.35L + E + 0.1I + 0.03S
(excluding depreciation and interest)
= 1.03R + 2.42L + 1.03E + 0.103I

b) Total manufacturing cost = R + 3.55L + E + 0.11I + Freight
(excluding depreciation and interest)

N. B. Add 0.1I to include depreciation, as quoted by Aries and Newton.

Holland [21]

a) Raw materials	R			
Operating labour	L			
Supervision, 10-25 % L	0.18L			
Utilities		E		
Maintenance, 6 % I			0.06I	
Royalties and patent costs 1-5 % S				0.035S
Payroll overhead, 15-20 % L	0.18L			
Laboratories, 10-20 % L	0.15L			
Plant overheads, 50-150 % L	1.00L			
Packaging, up to 33 % S				—
Property taxes or rates, 2 % I			0.02I	
Insurance, 1 % I			0.01I	

Total operating cost = R + 2.5L + E + 0.09I + 0.03S
(excluding depreciation and interest)
= 1.03R + 2.58L + 1.03E + 0.093I

b) Rapid method
Total operating costs = R + 2.25L + E + 0.09I
(excluding depreciation and interest)

CLARKE [27]

Total operating cost $= R + aL + E + bI$
(excluding depreciation and interest)

a and b are constants that are derived for specific situations.
Typically [28] $a = 2.30$ and $b = 0.1$ which gives:

$$= R + 2.30L + E + 0.1I$$

WELLS [25]

Raw materials	R			
Energy			E	
Catalysts and chemicals				
Wages, labour		L		
supervision, 25 % L		0.25L		
Maintenance, 3-10 % I				0.065I
General expenses, 3 % I				0.03I
Overheads, 3-4 % I				0.035I

Total operating cost $= R + 1.25L + E + 0.13I$
(excluding depreciation and interest)

JELEN [26]

a) Raw materials b) Byproduct and scrap credit	R				
c) Utilities			E		
d) Labour		L			
e) Supervision, 10-25 % L		0.18L			
f) Payroll charges, 15-25 % (d + e)		0.235L			
g) Maintenance, 3-6 % I				0.045I	
h) Operating supplies, 0.5-1.0 % I				0.008I	
j) Laboratory, 20 % L		0.2L			
k) Royalties, 1-5 % S					0.03S
l) Contingencies, 2-10 % (m)	.06R	0.097L	0.06E	0.003I	0.002S
m) *Direct production costs*	*1.06R + 1.712L*		*1.06E*	*0.056I + 0.032S*	
n) (Depreciation), 5-10 % I				(0.075I)	
o) Property taxes, 2 % I				0.02I	
p) Interest, 6-8 % I				0.07I	
q) Insurance, 1 % I				0.01I	
r) Plant overhead, 40-60 % L [OR 15-30 % (m)]		0.5L			
s) Indirect costs		0.5L		0.175I	
t) Packaging					
u) Labour					
v) Shipping, 1-3 % S					0.02S
w) Overhead, 50-75 % (u)					
x) Distribution costs					

Total operating cost $= 1.06R + 2.12L + 1.06E + 0.231I + 0.052S$
(including depreciation)

Total operating cost $= 1.06R + 2.212L + 1.06E + 0.156I + 0.052S$
(excluding depreciation)

$$= 1.12R + 2.33L + 1.12E + 0.1641I$$

Table 6

Comparison of total operating cost correlations

	Raw materials	+ Labour	+ Energy	+ Fixed investment	
Peters *et al.*	1.14R	+ 2.85L	+ 1.14E	+ 0.158I	= Total operating cost
Aries *et al.* a	1.03R	+ 2.42L	+ 1.03E	+ 0.103I	
b	R	+ 3.55L	+ E	+ 0.11I	
Holland *et al.* a	1.03R	+ 2.58L	+ 1.03E	+ 0.093I	
b	R	+ 2.25L	+ E	+ 0.09I	
Wells	R	+ 1.25L	+ E	+ 0.13I	
Jellen	1.02R	+ 2.33L	+ 1.12E	+ 1.164I	
Clarke	R	+ 2.30L	+ E	+ 0.1I	

(Depreciation and interest are excluded).

After consideration of the source and age of the above correlations, the following equation is suggested as being suitable for current estimates:

$$\text{Total operating cost} = 1.10R + 2.50L + 1.10E + 0.14I$$

(excluding depreciation and interest)

The correlation described earlier for labour and energy may be put into this equation, to either give a total operating cost per unit manufactured or on a daily or annual basis. It is hoped that this would give a reasonable order of magnitude estimate. As this has not yet been thoroughly tested, it should be treated with caution and any feedback from its use would be most welcome.

Following the work on relating specific operating costs to basic process parameters such as plant capacity, number of functional units and fixed investment, the following correlations for total operating cost have been developed for petrochemical processes [27]:

$$\text{Total operating cost} = R + 189.0I/Q$$

(excluding depreciation and interest)

$$\text{Total operating cost} = R + 312.0 \left(\frac{I}{Q}\right)^{0.961}$$

(including depreciation and interest)

A range of models were derived, some giving marginally greater accuracy at the expense of complexity, and other giving a total operating cost including raw materials. It is hoped to report further on this work and future developments in due course. Again these have not been tested and should be treated with caution — feedback and comments would be welcomed.

5 — CONCLUSIONS

The contribution of individual costs to total manufacturing cost have been illustrated and the significant areas identified. Techniques for estimating these individual costs are surveyed, including some recent correlations that relate labour and energy cost to basic plant/process parameters such as capacity, fixed investment and number of functional units. Overall operating cost correlations have also been derived, developed and surveyed, again including some models relating operating cost to basic plant/process parameters. There is clearly need for further work in improving the reliability and general applicability of such correlations, which are valuable not only for cost estimation but also for comparing an existing situation with standard costs to aid identification of areas of high cost.

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RESUMO

A justificação económica é, em geral, o factor mais importante a considerar no que respeita ao futuro de um projecto. É pois importante que os orçamentos de custos sejam tanto quanto possível exactos e de confiança. Tradicionalmente a avaliação de custos é dividida em custos de capital, ou fixos, e custos de operação, ou variáveis. Estes últimos podem, por seu turno, ser subdivididos de várias maneiras como o demonstram os exemplos de várias indústrias que se apresentam. Deste modo podem identificar-se as áreas onde os custos de operação são mais significativos, relacionando-as por sua vez através das técnicas tradicionais de avaliação de custos de operação. A partir deste tratamento desenvolvem-se técnicas rápidas e globais que se comparam com realizações recentes neste campo.

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CARDIOTONIC STEROIDS. SYNTHESIS OF CARDENOLIDES SULPHATES

Several sulphate derivatives of cardenolides with potential cardiotonic property were synthesised in good yields. A new sulphating agent, pyridine sulphate and dicyclohexylcarbodiimide in dimethyl formamide, was developed.

1 — INTRODUCTION

The formation of sulphate derivatives of cardenolides in the metabolic process of these important cardioactive compounds is well known both «in vivo» and «in vitro» [1]. Since these compounds were only synthesised by enzymatic methods [2] and were not isolated in a pure state for a full chemical characterisation, their chemical synthesis described herein were undertaken to provide authentic reference materials for biochemical studies, and to clarify the metabolic pathways involved in the excretion of these drugs as their sulphate esters.

Their importance as water-soluble potential cardiotonic drugs cannot but be stressed, since one the major limitations of the cardiotonic steroids is their low solubility in a aqueous medium. Also it was thought that a hydrophilic group like the sulphate, which is a natural metabolite, will improve its absorbance in the body fluid and its transport to the probable site of action in the myocardium [3].

2 — DISCUSSION OF RESULTS

The problem encountered in the sulphation of the more common cardenolides like digitoxigenin (I), digoxigenin (II), 3-epidigitoxigenin (III), 12-ketodigoxigenin (IV) and 3-ketodigoxigenin (V) is mainly the very facile elimination of the 14-hydroxy group to give the biologically inactive $\Delta^{14(15)}$ derivatives under mild dehydration conditions, the instability of the unsaturated lactone ring to basic reagents and the ease with which configurational inversion can occur at C-17 to give the 17-α-butenolide derivatives, under elevated temperatures [4].

The selective sulphation of digitoxigenin (I) at the 3β-OH was achieved in good yields in pyridine at room temperature, using an equimolar amount of pyridine sulphate and acetic anhydride, as an internal dehydrating agent [5]. The reaction monitored by t.l.c., was complete in 3 hours and no trace of other product could be detected, in a number of solvent systems.

The same 3β-sulpho-oxy derivative (VI) was also obtained in good yield from (I) by treatment with a new sulphating system, pyridine sulphate-dicyclohexylcarbodiimide, in dimethylformamide at room temperature.

When a two-fold excess of sulphating agent (pyridine sulphate-acetic anhydride) was used, it was noticed that the 3β-hydroxy group was sulphated in 30 minutes. After 2 hours an aliquot of the reaction mixture showed on t.l.c. the presence of the 3β-sulpho-oxy-$\Delta^{14(15)}$-digitoxigenin (VII) in *ca.* 10 %. After 20 hours, t.l.c. showed that the ratio of the $\Delta^{14(15)}$-compound (VII) relative to compound (VI) had increased to 40 %. This seems to indicate that subsequent to the rapid formation of the 3β-ester, the C-14 hydroxyl is converted to the tertiary sulphate, which rapidly eliminates to yield the olefin. Hydrolysis of (VII) with moist dioxan generated the 3β-hydroxyl without inversion and the resulting compound (VIII) was identical with an authentic sample of β-anhydrodigitoxigenin [6, 7]. 3β,12β-diacetoxydigitoxigenin (X), resists dehydration with phosphorus oxychloride in pyridine to the derivative (XI) under conditions that are effective for 3β-acetoxydigitoxigenin [8]. Clearly the 12β-acetoxy group sterically hinders the formation of the intermediate bulky 14-phosphate ester with the consequence that more vigorous conditions become necessary for its dehydration [8]. When the same compound (X) was treated with a 4-fold excess of pyridine sulphate-acetic anhydride at room temperature, a very slow elimination of the 14β-hydroxy group was found to occur. The 3,12-diacetoxy-β-anhydrodigoxigenin (XI) was isolated in 90 % yield after one week and found to be identical with an authentic sample. Epidigitoxigenin (III) prepared, by oxidation of digitoxigenin with chromium trioxide [9] followed by reduction with sodium borohydride in a aqueous dioxan [10], was esterified at the 3α-hydroxyl using equimolar amounts of pyridine sulphate-acetic anhydride at room temperature. The 3α-sulpho-oxy derivative (XIII) obtained in quantitative yield, was isolated as the pyridinium salt.

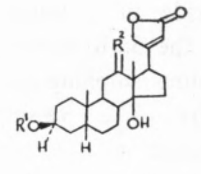
The compounds prepared in a similar fashion are listed in table 1.

The complete sulphation of digoxigenin (II) was next attempted by allowing the genin to react with two moles of the above sulphating agent. The pyridine salt of the 3β,12β-disulphate (XIV) was obtained in good yield as a transparent glass, which crystallised from dry dichloromethane on prolonged refrigeration.

The utility of the described method for the selective sulphation of digoxigenin (II) was next investigated. Reaction of equimolar amounts of this steroid and pyridine sulphate-acetic anhydride afforded a mixture of compounds found by t.l.c. to be composed mainly of 3β-and 12β-monosulphates. This seems to point out that the reactivities of the 3β-OH and the 12β-OH are very comparable [11]. Also the difficulty of separating the mixture of these two mono sulphates, by triangular crystallisation or chromatography, made this approach impractical. Attempted selective hydrolysis of the 12β-acetoxy in (XVI) or sodium borohydride reduction of the 12-keto group of (XV) to produce the 3β-sulpho-oxy derivative (XVIII) met only with partial sucess. This was due to the difficulty in obtaining the final product crystalline and free of impurities.

Table 1

Starting material	Product	m. p.	$[\alpha]_D$	$\lambda_{max}(\varepsilon)$
12-Ketodigoxigenin(IV) [12]	(XV)	116-8	+ 73 (*c* 0.11, MeOH)	217 (14 600) 255 (2 900)
12-Acetoxydigoxigenin(XX) [12]	(XVI)	134-7	+ 36 (*c* 0.69, MeOH)	215 (13 800) 254 (4 200)
Digoxigenin(II) [12]	(XIV)	125-7	+ 2 (*c* 0.27, MeOH)	218 (14 700) 256 (7 900)
3-Ketodigoxigenin(V) [22]	(XVII)	112-4	+ 5 (*c* 0.37, MeOH)	215 (15 500) 256 (4 300)



(I) $R^1 = H$, $R^2 = H, H$

(II) $R^1 = H$, $R^2 = \alpha\text{-}H, \beta\text{-}OH$

(IV) $R^1 = H$, $R^2 = O$

(VI) $R^1 = SO_3^- C_5H_6N^+$

(IX) $R^1 = (\text{digitoxose})_3$, $R^2 = H, H$

(X) $R^1 = Ac$, $R^2 = \alpha\text{-}H, \beta\text{-}OAc$

(XII) $R^1 = Ac$, $R^2 = H, H$

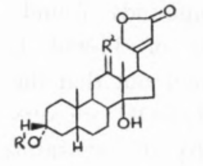
(XIV) $R^1 = SO_3^- C_5H_6N^+$, $R^2 = \alpha\text{-}H, \beta\text{-}SO_3^- C_5H_6N^+$

(XV) $R^1 = SO_3^- C_5H_6N^+$, $R^2 = O$

(XVI) $R^1 = SO_3^- C_5H_6N^+$, $R^2 = \alpha\text{-}H, \beta\text{-}OAc$

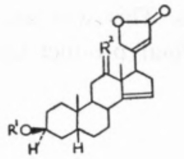
(XVIII) $R^1 = SO_3^- C_5H_6N^+$, $R^2 = \alpha\text{-}H, \beta\text{-}OH$

(XX) $R^1 = H$, $R^2 = \alpha\text{-}H, \beta\text{-}OAc$



(III) $R^1 = H$, $R^2 = H,H$

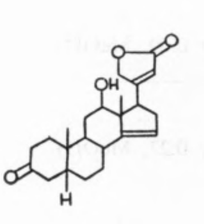
(XIII) $R^1 = SO_3^- C_5H_6N^+$, $R^2 = H,H$



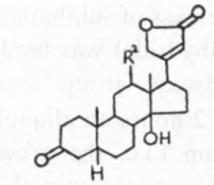
(VII) $R^1 = SO_3^- C_5H_6N^+$, $R^2 = H, H$

(VIII) $R^1 = H$, $R^2 = H, H$

(XI) $R^1 = Ac$, $R^2 = \alpha\text{-}H, \beta\text{-}OAc$

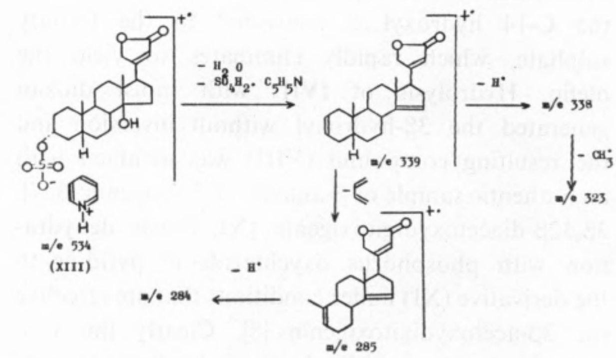


(XIX)

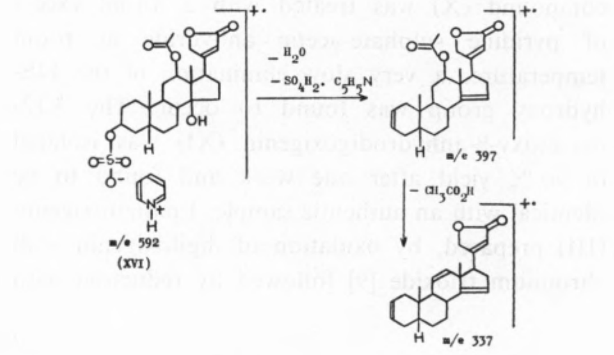


(V) $R^2 = \beta\text{-}OH$

(XVII) $R^2 = \beta\text{-}SO_3^- C_5H_6N^+$



Scheme 1

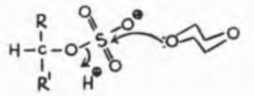


Scheme 2

Other methods of blocking the 12β-OH of (II) for specific sulphation of the 3β-hydroxyl, included the use of the very versatile trifluoracetoxy group. However when the model compound 3-ketodigoxigenin was reacted with trifluoracetic anhydride in pyridine, extensive dehydration ocurred at C-14 with formation of the β-anhydroderivative (XIX) on work up. That the major product was the $\Delta^{14(15)}$-anhydro compound, and not the isomeric $\Delta^{14(8)}$ olefin emerged from comparisons of the optical rotations of a series of closely related olefins. The negative value obtained for the optical rotation (— 20 in $CHCl_3$) is characteristic of the $\Delta^{14(15)}$-olefins [8].

All sulphates, analysed as their pyridinium salts, gave correct microanalysis as anhydrous salts and could, in general be easily crystallised from dry dichloromethane. Their infrared and ultraviolet spectra fully supported the structures postulated.

On hydrolysis, in aqueous dioxan, they afforded the parent genin showing that cleavage of the sulphate ester S-O predominates. In no instance could any epimeric products at the carbons C-3 and C-12 be observed. This fact is in full agreement with Goren's mechanism [13] for the hydrolysis, provided that minute amounts of electrophilic reagents are present in the reaction mixture.



The use of moist dioxan in the sulphate ester hydrolysis is well generalized after the investigation of McKenna and Norymberski [14] and was always used by us a control reaction, against dehydration of the steroid nucleus at C-14 during the sulphation reaction.

Due to the ever increasing use of mass spectra to identify natural metabolites, we decided to investigate the mass spectra of two representative sulphates of the cardenolides series, i.e. 3α-sulpho-oxy-digitoxigenin and 3β-sulpho-oxy-12β-acetoxy-digitoxigenin.

Characteristically none of these sulphates showed any detectable molecular ion, probably due to thermally induced salt decomposition [15]. The main peaks observed in the spectra could be easily accounted by Scheme 1. Dehydration [16, 17, 18] and sulphate elimination [15] in the spectra of (XIII) lead to the ion m/e 339 which then can undergo a retro Diels-Alder reaction [19] leading to m/e 285 and then by loss of a hydrogen to the most abundant peak in the spectrum at m/e 284. The presence of an acetate group at C-12 lead to a weak ion at m/e 397 which probably then looses acetic acid [19] leading to the appearance of a peak at m/e 337 (scheme 2). This ion then probably breaks down by a mechanism similar to the one depicted in Scheme 1. Other fragments at m/e 79, 64 and 48 were atributed to $C_5H_5N^+$, SO_2^+ and SO^+ respectively.

In conclusion, methods of synthesis of cardenolides sulphates were developed and their physical and chemical properties studied. These might be of considerable importance since the ready availability of authentic samples of these derivatives might simplify considerably biochemical studies involving their metabolism in man. Furthermore, the replacement of the sugar moiety in digitoxin by a hydrophilic group such as the sulphate, while probably retaining the cardiac activity which is associated with the aglycone, might improve the drugs absorbance and protect them against rapid liver metabolism and consequent inactivation [20].

3 — EXPERIMENTAL

Melting points are uncorrected and were taken with a temperature rise of 2° per minute on a model Leitz GMBH. I.r. spectra unless stated otherwise were determined in potassium bromide discs on a Perkin-Elmer Model 257. U.v. spectra were determined in methanolic solutions on a Beckman Model Acta CIII. Mass spectra were obtained with a M. S. 9 high resolution mass spectrometer using direct sample injection. Thin layer chromatography was carried out on Silica Gel G 254 (Merck) plates, 0.30 mm thick. For preparative work these were 0.5 mm thick. Microanalyses were performed at Alfred Bernhardt's Mikroanalytisches Laboratorium.

3.1 — *3β-SULPHO-OXY-14β-HYDROXY-5β-CARD-20(22)-ENOLIDE (PYRIDINIUM SALT) (VI)*

Method A

Pyridine sulphate (57.0 mg) in dry pyridine (0.5 ml) containing acetic anhydride (0.05 ml) was stirred at room temperature for 20 minutes. Digitoxigenin (90.7 mg) in pyridine (1.0 ml) was added and the mixture stirred at room temperature for 3 hrs. The addition of light petroleum (10 ml) precipitated the product as an oil which was crystallised from dichloromethane-ethyl acetate to give *the pyridinium salt* (VI) as white needles (103.5 mg, 80 %),

m.p. 139-142,
$[\alpha]_D^{28\cdot5} + 9.6$ (*c* 0.25, MeOH)
λ_{max} 218.5 (ε15579) and 256 nm (3895),
ν_{max} 3442, 3300-3000, 2561, 1801, 1738, 1623, 1546, 1487, 1258, 1048, 818 and 692 cm^{-1}.
(Found: C, 62.7; H, 7.3; N, 2.6; S, 5.8 %. $C_{28}H_{39}NO_7S$ requires C, 63.0; H, 7.4; N, 2.6; S, 6.0 %).

Method B

Pyridine sulphate (9.94 mg) in dry dimethylformamide (0.5 ml) and dicyclohexylcarbodiimide (36.9 mg) were stirred at room temperature for 7 min. Digitoxigenin (20.8 mg) in dry dimethylformamide (0.2 ml) was added. The reaction of sulphation of the 3-hydroxy group was found to be complete in 10 min. (t.l.c. control). The solvent was removed under high vacuum and the residue purified by triangular crystallisation from dichloromethane to give the *pyridinium salt* (VI) (58 %) identical in all respects with the material obtained by method A.

Method C

Pyridine sulphate (21.8 mg) in dry pyridine (0.5 ml) and acetic anhydride (0.015 ml) were stirred at room temperature for 30 min. Digitoxigenin (20.5 mg) was added and the mixture stirred at room temperature for 30 minutes, during which, time complete esterification of the 3-hydroxy group had occurred and no trace of the 3-sulphate derivative of *β-anhydrodigitoxigenin* (VII) could be detected (t.l.c. control). After 2 hrs. the product from an aliquot was worked up in the usual manner and hydrolysed with aqueous dioxan to give digitoxigenin (I) and the β-anhydro compound (VIII) in a ratio *ca.* 9 : 1. Continued stirring for 20 hours yielded the anhydro compound in 40 % yield.

3.2 — *3β,12β-DIACETOXY-5β-CARD-14(15)-20(22)-DIENOLIDE (XI)*

Pyridine sulphate (164 mg), acetic anhydride (0.2 ml) and pyridine (1 ml) were stirred at room temperature for 45 min. 3,12-diacetoxy-14β-hydroxy-5β-card-20(22)-enolide (X) (100 mg) was added and the reaction was allowed to proceed at room temperature for 8 days.

The reaction mixture was acidified with 2 % aq. sulphuric acid (10 ml), extracted with chloroform (4 × 10 ml), washed with water (10 ml), dried (Na_2SO_4) and the solvent removed under reduced pressure to yield a yellow gum which on purification by column chromatography, using chloroform-methanol (100 : 2) afforded pure 3,12-diacetoxy-5β-card-14(15)-20(22)-dienolide (XI) (86 mg, 90 %), m.p. 193-196 (lit. [8] m.p. 197-198) $[\alpha]_D^{24\cdot5} + 30$ (*c* 0.37, $CHCl_3$) (lit. [8] $[\alpha]_D + 30.8$ ($CHCl_3$)). The i.r. spectrum showed no absorption due to hydroxyl group and was found to be identical with a sample prepared by dehydration of digoxigenin followed by acetylation [21].

3.3 — *3α-SULPHO-OXY-14β-HYDROXY-5β-CARD-20(22)-ENOLIDE (PIRYDINIUM SALT) (XIII)*

The sulphate prepared in a similar manner, by *method A*, except for the reaction time which was reduced to 50 min. (XIII) was isolated with light petroleum (100 %) and crystallised as white needles from dichloromethane-ethylacetate

m.p. 115-118,
$[\alpha]_D^{28\cdot5} + 25$ (*c* 0.26, MeOH),
λ_{max} 218.5 (ε 14 170) and 256 nm (3 490),
ν_{max} 3477, 1782, 1741, 1631, 1617, 1533, 1250-1200, 755 and 684 cm^{-1},
m/e 339, 338, 336, 334, 323, 284 (100 %), 79, 64, 48.
(Found: C, 62.9; H, 7.3: N, 2.8; S, 6.1 %.
$C_{28}H_{39}NO_7S$ requires: C, 63.0; H, 7.4; N, 2.6; S, 6.0 %).

3.4 — *3β-SULPHO-OXY-12β-ACETOXY-14β-HYDROXY-5β-CARD-20(22)-ENOLIDE (PYRIDINIUM SALT) (XVI)*

The sulphate was prepared in the usual manner. The *pyridinium salt* (XVI) was isolated in almost quantitative yield as white needles m.p. 134-137 (from dichloromethane),

$[\alpha]_D^{28.5}$ + 36.4 (*c* 0.69, MeOH),
λ_{max} 223 (ε 11 370) and 256 nm (5 580),
ν_{max} 3433, 3300-3040, 1779, 1742, 1717, 1626, 1622, 1544, 1487, 1232, 1183 cm^{-1},
m/e 396, 354, 337, 336 (100 %), 334, 332, 321, 319, 317, 282, 280, 278, 228, 226, 79, 64, 48.
(Found: C, 60.7; H, 6.8; N, 2.55; S, 5.6 %. $C_{30}H_{41}NO_9S$ requires: C, 60.9; H, 7.0; N, 2.4; S, 5.4 %).

3.5 — *3β-SULPHO-OXY-12-KETO-14-HYDROXY-5β-CARD-20(22)-ENOLIDE (PYRIDINIUM SALT) (XV)*

The sulphate was prepared in the usual way. The pyridinium salt (XV) obtained in an almost quantitative yield was crystallised from dichloromethane-light petroleum as white needles m.p. 116-119,

$[\alpha]_D^{23.5}$ + 73 (*c* 0.108, MeOH),
λ_{max} 217 (ε 14 600) and 255 nm (2 860),
ν_{max} 3465, 3150-3050, 1797, 1761, 1695, 1630, 1533, 1491, 1247, 1059 and 679 cm^{-1}.
(Found: C, 61.2; H, 6.7; N, 2.7; S, 5.7 %. $C_{28}H_{37}NO_8S$ requires: C, 61.4; H, 6.8; N, 2.6; S, 5.85 %).

3.6 — *3β,12β-DISULPHO-OXY-14β-HYDROXY-5β-CARD-20(22)-ENOLIDE (PYRIDINIUM SALT) (XIV)*

Pyridinium sulphate (49.6 mg) in dry pyridine (0.5 ml) containing acetic anhydride (0.05 ml) was stirred at room temperature for 30 minutes. Digoxigenin (50 mg) in pyridine (0.8 ml) was added and the reaction took 3 $^1/_2$ hours for completion. Addition of petroleum ether (4 ml) precipitated the crude pyridinium salt of *digoxigenin disulphate* (XIV) (100 mg), which afforded small colourless crystals

m.p. 125-127 (CH_2Cl_2), $[\alpha]_D^{28.5}$ + 2 (*c* 0.27, MeOH),
λ_{max} 218 (ε 14 700) and 256 nm (7 900),
ν_{max} 3446, 1776, 1741, 1632, 1616, 1534, 1250-1200, 754 and 685 cm^{-1},
m/e 354, 337, 336 (100 %), 334, 332, 321, 319, 317, 282, 280, 278, 226, 79, 64, 48.
(Found: C, 55.7; H, 6.4; N, 4.1; S, 9.3 %. $C_{33}H_{44}N_2O_{11}S_2$ requires: C, 55.9; H, 6.3; N, 4.0; S, 9.0 %).

3.7 — *12β-SULPHO-OXY-3-KETO-14β-HYDROXY-5β-CARD-20(22)-ENOLIDE (PYRIDINIUM SALT) (XVII)*

Pyridine sulphate (46 mg) in pyridine (1 ml) containing acetic anhydride (0.05 ml) was allowed to stand at room temperature for 30 minutes. 3-keto--12β,14β-dihydroxy-5β-card-20(22)-enolide (84 mg) in pyridine (2.5 ml) was added and the reaction allowed to proceed at room temperature for 2 hours (t.l.c. control).
Light petroleum (15 ml) was added and the precipitated oil dried and crystallised from dichloromethane-light petroleum to afforded *white rosettes* (101 mg) of the *12β-sulphate* (XVII),

m. p. 112-114,
$[\alpha]_D^{28.5}$ + 5 (*c* 0.37, MeOH),
λ_{max} 215 (ε 15 500) and 253 nm (4300),
ν_{max} 3440, 1779, 1744, 1711, 1260-1170, 754 and 683 cm^{-1}.
(Found: C, 61.5; H, 6.9 %. $C_{28}H_{37}NO_8S$ requires: C, 61.4; H, 6.8 %).

When this sulphate was solvolysed in dioxan/water the parent genin was obtained in almost quantitative yield.

3.8 — *DEHYDRATION OF 3-KETO-12β,14β-DIHYDROXY-5β-CARD-20(22)-ENOLIDE*

The ketone (V) (109 mg) was refluxed with ethanol (15 ml) containing conc. sulphuric acid (1.0 ml) and water (10 ml) for 5 hours. The solvents were removed under reduced pressure, leaving a white precipitate which was filtered and purified by column chromatography using dichloromethane: methanol (100 : 2) as eluent. 3-keto-12β-hydroxy-5β-card-14(15)-20(22)-dienolide (XIX) was separated (71.1 mg) and crystallised from dichloromethane-acetone: petroleum to yield small white crystals,

m.p. 252-255 (dec.), $[\alpha]_D^{28\cdot5}$-20 (*c* 0.136, $CHCl_3$),
λ_{max} 215 (ε 15 500) and 256 nm (4 300),
ν_{max} 3576, 3416, 3047, 1795, 1736, 1714 and 1626 cm^{-1}.
(Found: C, 74.4; H, 8.3 %. $C_{23}H_{30}O_4$ requires: C, 74.6; H, 8.2 %).

3.9 — *3-KETO-12β-HYDROXY-5β-CARD-14(15)-20(22)-ENOLIDE (XIX)*

To a solution of ketone (V) (150 mg) in pyridine (2 ml) was added trifluoracetic anhydride (0.5 ml) at 0 °C. The reaction was allowed to proceed for one hour until completion, and then mixed with ice-water. The white precipitate was filtered, washed with dilute aqueous solution of sodium bicarbonate and dried. Crystallisation ob the crude material (144 mg) from acetone-petroleum ether afforded 3-keto-12β-hydroxy-5β-card-14(15)-20(22)-dienolide (XIX), m.p. 255-257.5 (dec.), $[\alpha]_D^{28\cdot5}$-20 (*c* 0.136, $CHCl_3$), found to be identical in all respects with the anhydro compound prepared by the sulphuric acid/ethanol dehydration previously described.

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RESUMO

Vários sulfatos com propriedade cardiotónica potencial foram sintetizados com bons rendimentos. Desenvolveu-se um novo reagente de sulfatação: sulfato de piridínio e diciclo-hexilcarbodi-imida em dimetilformamida.

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MECHANISMS OF THE INTERACTION BETWEEN EXCITED URANYL IONS AND ORGANIC MOLECULES (1)

The mechanisms of deactivation of the lowest excited state of uranyl ion by organic molecules are discussed. Rates of interaction between excited uranyl ion and alchols are measured by flash photolysis and luminescence quenching and are found to be sensitive both to the structure of the alcohol and to deuteration. E. S. R. evidence suggests that this interaction involves hydrogen atom abstraction from the substrate by $(UO_2^{2+})^*$*. Further studies are reported on the interaction between excited uranyl ion and carboxylic acids, ethers, alkenes and alkyl halides, and it is suggested that quenching of* $(UO_2^{2+})^*$ *by these species is effected by a variety of processes including exciplex formation, heavy atom effects, and chemical quenching.*

Although the ability of the uranyl ion, UO_2^{2+}, to photosensitise the oxidation of a large variety of organic molecules has been known for many years [1], there remain many unresolved problems as to the detailed mechanism, which is probably different for different varieties of substrate. The primary photochemical processes of the initially excited states occur on a very fast time-scale (10^{-9} to 10^{-6} s) and only comparatively recently have direct studies of the rate processes of excited uranyl ion become feasible by such techniques as μs and ns flash photolysis and single photon counting. The purpose of this account is to describe the applications of these techniques and others to the problem of uranyl ion photochemistry which have been performed at Warwick over the last few years, noting how the results have been confirmed (and sometimes anticipated) by groups working in Japan and the U.S.S.R.

The first aim was to obtain some absolute rate constants for the attack of $(UO_2^{2+})^*$ upon certain 'model' substrates such as methanol. Now it has been possible for MATSUSHIMA and his colleagues [2] to examine the quenching of the well known green luminescence of $(UO_2^{2+})^*$ by added alcohols by conventional spectrofluorimetry using the Stern-Volmer analysis of the data to yield a line of slope K_{SV} in dm^3 mol^{-1} where K_{SV} is the Stern-Volmer quenching constant, i.e., the product τk_2 where τ is the unquenched lifetime of $(UO_2^{2+})^*$ and k_2 is the absolute rate constant for attack of $(UO_2^{2+})^*$ upon substrate. This approach, while most useful in affording primary kinetic isotope effects (and thereby indicating the principal site of attack of $(UO_2^{2+})^*$ upon substrate to be a C-H bond in a CH_2OH or CHOH group) and also the effect of structural variation upon reactivity, suffers nonetheless from yielding essentially composite data.

To obtain some values for absolute rate constants, we first measured directly the decay of the photoreactive state of UO_2^{2+}, both in emission by single-photon counting and in absorption by monitoring the excited-state *absorption* previously detected on flash photolysis of UO_2^{2+} -doped silicate glass [3]. This appeared at $\lambda_{max} \sim 570$ nm on μs flash photolysis of uranyl salts in a variety of fluid

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(1) Lecture presented at Laboratório Químico da Universidade de Coimbra in May 1974.

media including H_2O, D_2O, H_2SO_4 and 50 % $HClO_4$-50 % H_3PO_4 [4], exhibiting vibronic structure in all cases with an averaged band separation of about 580 cm^{-1} (fig. 1) and agrees with the liquid phase spectrum of RYGALOV and colleagues [5]. Its decay in water was too fast for conventional flash equipment, however, and instead a 50 ns flash from a ruby-doubled laser was employed as excitation source. Excellent first-order kinetics were then obtained for the decay of the 570 nm absorption with $k_1 (H_2O) = 8.02 \times 10^5 s^{-1}$ and $k_1 (D_2O) = 4.20 \times 10^5 s^{-1}$; the isotope effect of 1.91 accords with the measured 1.7 to 2.0-fold greater luminescence intensity of UO_2^{2+} ion in D_2O compared with H_2O [4, 6]. The general magnitude of the decay constant of $(UO_2^{2+})^*$ was confirmed by single-photon counting experiments to be $(4.3 \pm 0.5) \times 10^5 s^{-1}$, although we would not regard this figure to be quite as reliable as that based on the laser flash photolysis experiments.

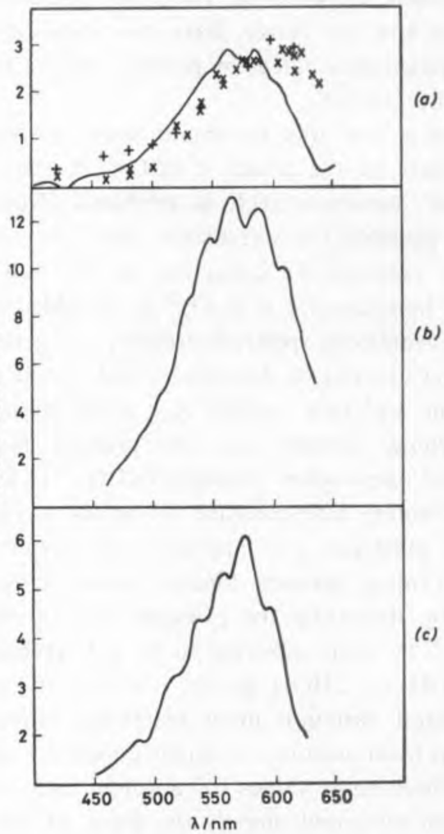


Fig. 1

Flash photolysis spectra of solutions of uranyl salts: (a) full line, spectrographic recording of absorption from 20 m mol dm^{-3} uranyl perchlorate in water following μs flash; X, photoelectrically recorded absorptions on laser flashing 20 m mol dm^{-3} aqueous uranyl perchlorate; +, analogous experiments with uranyl nitrate; (b) microsecond (spectrographic) spectrum from 20 m mol dm^{-3} aqueous uranyl sulphate; (c) low temperature (215 K) microsecond (spectrographic) spectrum from 20 m mol dm^{-3} uranyl perchlorate in 50/50 (v/v) H_3PO_4 + + $HClO_4$. (Reproduced with permission from Ref. 4)

The demonstration of an energy level positioned 17 400 cm^{-1} above the first excited state of UO_2^{2+} (itself at 21 329 cm^{-1}) accords with the observation of a level at 36 873 cm^{-1} in the absorption spectrum of ground state UO_2^{2+} [7]. The relatively intense nature of the 570 nm absorption implies that the transition is «allowed» in character and, accepting that the lowest excited state (centred at 24 107 cm^{-1}) is triplet in character [8] then the absorption is of a T-T nature. The lower excited states of UO_2^{2+} can therefore be represented in a simplified term diagram (fig. 2).

The lifetime of the 570 nm absorption is progressively reduced on addition of a variety of normal and deuteriated alcohols, plots of k_1 (the pseudo-first order rate constant) versus alcohol concentration giving in all cases good straight lines with an intercept on the rate axis corresponding to the decay in pure water. The slopes of these plots yield k_2, the absolute rate constant for the interaction between $(UO_2^{2+})^*$ and the alcohol. Representative values of k_2 are compiled in Table 1. Evidently k_2 is sensitive to the structure of the alcohol and to the exact site of deuteriation, the substantial CH/CD isotope effect indicating the interaction to involve considerable stretching of the C-H bond in the transition state, and presumably complete breakage on completion of the reaction. The value of k_H/k_D is quite comparable with those for the oxidation of a number of alcohols by strong one-electron oxidising agents such as Ce(IV), Co(III) and Cr(IV) [9]. These trends were confirmed in the case of methanol by single-photon counting, when the luminescence decay of $(UO_2^{2+})^*$ was accelerated by added CH_3OH and CD_3OH to yield

$$k_2[(UO_2^{2+})^* + CH_3OH] = (4.48 \pm 0.08) \times \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_2[(UO_2^{2+})^* + CD_3OH] = (1.73 \pm 0.13) \times \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

i.e., $k_H/k_D = 2.6 \pm 0.2$.

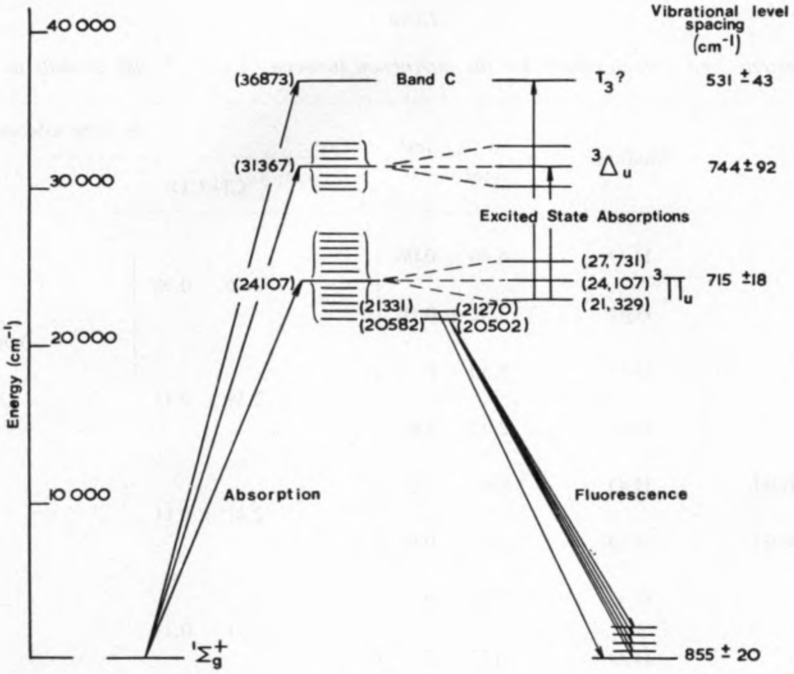
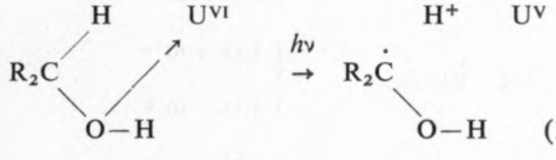


Fig. 2

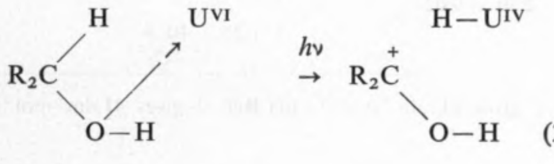
Energy level diagram for lower excited states of UO_2^{2+} ion (based on data and assignments of Bell and Biggers, Ref. 7 and 8, and on excited state absorption studies of Ref. 4)

These results correlate very well with those obtained by MATSUSHIMA [2] for quenching of the integrated luminescence intensity of UO_2^{2+} by added alcohols, together with our own measurements using the same approach. Division of the resulting values for K_{SV} by the absolute values for k_2 (of Table 1) yields an approximately constant figure of 10^{-6} s, which corresponds to the radiative lifetime τ, in good agreement with the independent value for $1/\tau$ of $8.02 \times 10^5\ s^{-1}$ obtained directly.

Although it is clear from these results that $(UO_2^{2+})^*$ is quenched by alcohols as a result of chemical interaction, it is not clear whether the chemical act is one of hydrogen atom abstraction (equation 1) or of hydride-ion transfer (equation 2).

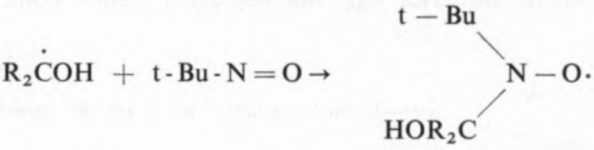


$$\mathrm{R_2C(H)(O{-}H)\quad U^{VI} \xrightarrow{h\nu} H^+\quad U^{V}\quad R_2\dot{C}{-}O{-}H} \qquad (1)$$



$$\mathrm{R_2C(H)(O{-}H)\quad U^{VI} \xrightarrow{h\nu} H{-}U^{IV}\quad R_2\overset{+}{C}{-}O{-}H} \qquad (2)$$

However, (1) must be favoured at present in view of the successful identification by e.s.r. of the resulting alcohol radical both by inducing the photoreaction in a solid matrix at 77 K [10] or in very cold solution [11], and also by using a spin-trapping reagent



$$\mathrm{R_2\dot{C}OH + t\text{-}Bu\text{-}N{=}O \rightarrow (t{-}Bu)(HOR_2C)N{-}O\cdot}$$

followed by e.s.r. measurement of the resulting nitroxide radical [12].

The other groups of organic molecules we have examined are carboxylic acids, ethers, alkenes and alkyl halides. We began with carboxylic acids, which have been stated (1) to be decomposed by $(UO_2^{2+})^*$ by a «sensitised» mechanism involving no net loss of U(VI), viz.

$$RCO_2H + (UO_2^{2+})^* \rightarrow RH + CO_2 + UO_2^{2+} \qquad (3)$$

i.e., either no radical intermediate $-U^V$ pair is formed or, if it is produced, then a ready re-oxidation pathway exists for U^V. *Some* organic

Table 1

Rate constants and isotope effects for the interaction between $(UO_2^{2+})^*$ and alcohols at 293 K

Alcohol	Medium	$10^{-6}k_2$/dm^3 mol^{-1}s^{-1}	Isotope effects CH/CD	Isotope effects OH/OD
CH_3OH	H_2O	6.40 ± 0.08	2.76 ± 0.98	0.98
CD_3OH	H_2O	2.32 ± 0.10		0.85
CH_3OD	D_2O	6.50 ± 0.19	2.39 ± 0.11	
CD_3OD	D_2O	2.72 ± 0.04		
$(CH_3)_2CHOH$	H_2O	85.3 ± 1.5	2.41 ± 0.11	
$(CH_3)_2CDOH$	H_2O	35.4 ± 0.9		
c-$C_6H_{11}OH$	H_2O	294 ± 9	2.31 ± 0.12	
c-$C_6D_{11}OH$	H_2O	127 ± 3		

radicals are produced and can be detected by e.s.r. in solid matrices [10] or solution [11] but these could be derived from a minor pathway. No Stern-Volmer data existed for the interaction between simple carboxylic acids and $(UO_2^{2+})^*$ and we examined [13] a suitably wide range of acids (Table 3). In the series of unsubstituted acids, alkylation of the methyl protons of acetic acid rapidly increases K_{SV}, but beyond a certain point this effect maximises: with cyclic acids, however, K_{SV} is uniformly an order-of-magnitude higher. Substitution by halogen atoms produces some striking effects: that of CH_3CO_2H by Cl or Br has relatively little effect, but I enormously increases K_{SV}, suggesting at once a heavy-atom (spin-orbit) perturbation of the luminescence, and a separate experiment using ethyl iodide as quencher (in acetone-water solvent) yielded a quenching constant

Table 2

Stern-Volmer constants (K_{SV}) for the quenching of $(UO_2^{2+})^*$ luminescence by added alcohols

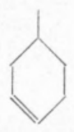
Alcohol	K_{SV} dm^3 mol^{-1}	K_{SV}^H/K_{SV}^D	K_{SV}/k_2[a]
CH_3OH	5.26 ± 0.03 (*b*)	2.76 ± 0.05	0.82×10^{-6}
CD_3OH	1.90 ± 0.02		0.82×10^{-6}
$(CH_3)_2CHOH$	96.5 ± 0.3 (*c*)	2.42 ± 0.02 (*e*)	1.13×10^{-6}
$(CH_3)_2CDOH$	39.9 ± 0.2 (*d*)		1.13×10^{-6}
c-$C_6H_{11}OH$	369 ± 2	2.30 ± 0.02	1.25×10^{-6}
c-$C_6D_{11}OH$	160 ± 1		1.26×10^{-6}

(*a*) Data from Table 1; (*b*) Ref. 2 gives 12 dm^3 mol^{-1}; (*c*) Ref. 2 gives 113 dm^3 mol^{-1}; (*d*) Ref. 2 gives 41 dm^3 mol^{-1}; (*e*) Ref. 2 gives 2.76.

Table 3

Stern-Volmer constants (K_{SV}) for the quenching of (UO_2^{2+}) by carboxylic acids (RCO_2H)*

Conditions: [UO_2^{2+}] (nitrate) = 0.02 mol dm^{-3}, [$HClO_4$] = 0.382 mol dm^{-3}
T = 290 K, Solvent: water or 48 % acetone-water (AA)

R	$K_{SV}{}^{H_2O}$ /dm^3 mol^{-1}	$K_{SV}{}^{AA}$ /dm^3 mol^{-1}	$10^{-6}k_2$ (derived) (*a*)/ /dm^3 mol^{-1} s^{-1}
H	6.5		6.0
CH_3	0.28		0.26
CD_3	0.28		0.26
CH_3CH_2	1.28	0.14	1.19
$CH_3CH_2CH_2$	1.91	0.41	1.78
$(CH_3)_2CH_2$	5.50		5.1
$CH_3CH_2CH_2CH_2$	—	3.27	—
$(CH_3)_2CHCH_2$	4.87		4.5
$(CH_3)_3C$	3.75	0.81	3.5
$(CH_3CH_2)_2CH$	15.0		1.40
$CH_3CH_2CH_2CH_2CH_2$	—	8.67	—
c-C_3H_5	6.1		5.7
c-C_4H_7	16.7		15.5
c-C_5H_9	49.5		46.1
c-C_6H_{11}	89.2	14.5	82.9
$ClCH_2$	0.15		0.14
$BrCH_2$	0.32		0.30
ICH_2	3 600	550	3 350
F_3C	enhancement		—
Cl_3C	enhancement		—
CH_3CHCl	18.4		17.1
$ClCH_2CH_2$	20.0		18.6
CH_3CHBr	103		96
$BrCH_2CH_2$	90		84
ICH_2CH_2	1 960		1 820
CH_3CH_2CHBr	36		34
$C_2H_5OCH_2CH_2$	203	71	189
$CH_3OCH_2CH_2$		37	
$CH_3CH = CH$	8.7	6.1	8.1
	—	8.4	—
$CH_2 = CHCH_2$	1 600	240	1 490
$CH_2 = CHCH_2CH_2$	—	1 520	—
HO_2CCH_2	enhancement		—
C_6H_5	4 150	1 750	3 860

(continues)

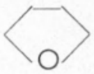
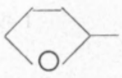
Table 3 (continued)

R	$K_{SV}^{H_2O}$ /dm³ mol⁻¹	K_{SV}^{AA} /dm³ mol⁻¹	$10^{-6}k_2$ (derived) (*a*) /dm³ mol⁻¹ s⁻¹
$p\text{-}\overset{+}{N}H_3C_6H_4$	920		860
$p\text{-}NO_2C_6H_4$	900		840
$m\text{-}NO_2C_6H_4$	850		790
$o\text{-}NO_2C_6H_4$	790		730
$p\text{-}FC_6H_4$	3 800		3 530
$m\text{-}ClC_6H_4$	2 030		1 890
$p\text{-}BrC_6H_4$	2 900		2 700
$o\text{-}IC_6H_4$	3 880		3 610
$p\text{-}CH_3C_6H_4$	4 380		4 070
$m\text{-}CH_3C_6H_4$	4 100		3 810
$o\text{-}CH_3C_6H_4$	3 400		3 160
$p\text{-}OCH_3C_6H_4$	6 000		5 580
$C_6H_5CH_2$	3 500		3 260
$(C_6H_5)_2CH$		2 260	—
$C_6H_5CH(OH)$		723	—

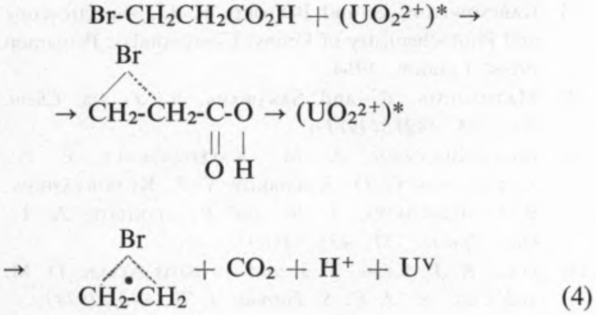
(*a*) 9.3 × 10⁵ $K_{SV}^{H_2O}$ (see text).

Table 4

Stern-Volmer constants (K_{SV}) for the quenching of $(UO_2^{2+})^*$ by ethers (Conditions and nomenclature as for Table 3)

Ether	$K_{SV}^{H_2O}$ /dm³ mol⁻¹	K_{SV}^{AA} /dm³ mol⁻¹	$10^{-6}k_2$ (derived) (*a*) /dm³ mol⁻¹ s⁻¹
$C_2H_5OC_2H_5$		138	—
$CH_3OCH_2CH_2OCH_3$	204		190
$(CH_3OCH_2CH_2)_2O$	327		304
	243		226
	547		509
	595		553
$(CH_3)_2CHOCH(CH_3)_2$		54	
$C_2H_5OCH_2CH_2CO_2H$	203	71	189
$CH_3OCH_2CH_2CO_2H$	—	37	—

of 670. The effect of iodine is also clear from the result with 3-iodopropionic acid, but the other Cl- and Br- substituted propionic acids also yield quite high quenching constants. Those with the 3-substituted propionic acids could be taken as evidence for stabilisation of bridged radicals, viz.



$$Br\text{-}CH_2CH_2CO_2H + (UO_2^{2+})^* \to$$

$$\to \overset{Br}{CH_2\text{-}CH_2}\text{-}\underset{\substack{\| \\ O}}{C}\text{-}\underset{\substack{| \\ H}}{O} \to (UO_2^{2+})^*$$

$$\to \overset{Br}{\dot{C}H_2\text{-}CH_2} + CO_2 + H^+ + U^V \qquad (4)$$

but (4) cannot operate for the equally strongly quenching 2-halo-acids. The strongly quenching behaviour of the two 3-alkoxypropionic acids investigated cannot be related to physical quenching, however, and we were initially inclined to take this as good evidence for a «bridge-stabilised» radical: examination of some simple ethers however (Table 4) showed that these are extremely good quenchers of $(UO_2^{2+})^*$ and that the origin of the quenching of the alkoxyacids probably lies in their ether function [13]. Another surprise came from the unsaturated acids; whilst two of these gave «normal» figures for K_{SV}, vinylacetic and 4-pentenoic acids gave $K_{SV} > 1500$, and again we initially regarded this as evidence for the intermediacy of resonance-stabilised radicals, e.g., the allyl radical from vinylacetic acid,

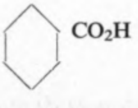
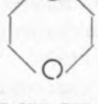
$$CH_2 = CH - CH_2 - CO_2H \to (U^{VI})^* \to$$

$$\to \overline{CH_2 - \dot{C}H - CH_2} + CO_2 + H^+ + U^V$$

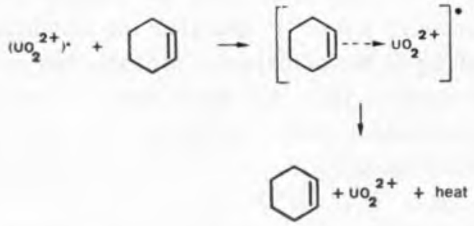
However, investigation of a simple alkene (cyclohexene) also afforded a large value for K_{SV}, implying an exciplex quenching mechanism of the type found by MATSUSHIMA [14] for a range of aromatic hydrocarbons with $(UO_2^{2+})^*$ and which

Table 5

Quantum yields for U(IV) appearance in the photo-oxidation of organic molecules by $(UO_2^{2+})^*$
Conditions: $[U(VI)] = 0.04$ M, $[HClO_4] = 0.382$ M, 5 cm cell, blue filter combination

Substrate	Concentration/ mol dm^{-3}	Medium	φ[U(IV)]	$10^{-6}k_2H_2O$ /dm^3 mol^{-1} s^{-1}
△ CO_2H	0.334	48 % acetone-H_2O	0.041	—
△ CO_2H	0.334	H_2O	0.037	52
 CO_2H	0.150	48 % acetone-H_2O	0.075	118
$BrCH_2CH_2CO_2H$	0.50	H_2O	$< 10^{-4}$	84
$C_2H_5OCH_2CH_2CO_2H$	1.20	H_2O	1.89	189
	1.17	H_2O	0.76	226
$CH_3OCH_2CH_2OCH_3$	1.08	H_2O	0.72	190
$(CH_3OCH_2CH_2)_2O$	0.295	H_2O	0.67	304

is reproduced in Table 3 for a wide range of aromatic carboxylic acids, viz.



The simplest discrimination between «physical» and «chemical» quenching is measurement of the yields of reaction products as far as possible. It is particularly easy to follow the fate of the reduced U(V) species as these disproportionate [15] to U(VI) + + U(IV), and the latter has a characteristic blue colour ($\lambda_{max} \sim 648$ nm $\varepsilon_{max} \sim 58$ $dm^3\ mol^{-1}\ cm^{-1}$). We measured φ[U(IV)] for several of our most reactive systems judged from values of K_{SV} (Table 5). Clearly the exceptionally high K_{SV} for ethers and cyclic acids is matched by high photochemical reactivity, but φ[U(IV)] for 3-bromopropionic acid is *not* high, confirming our supposition that the high K_{SV} for this acid has a purely physical origin.

The figures for K_{SV}/k_2 of Table 2 yield a mean value of 1.07×10^{-6} s for the natural lifetime of $(UO_2^{2+})^*$, i.e., k_1 (decay) = $9.3 \times 10^5\ s^{-1}$. Inserting this value for k_1 into all the other Stern-Volmer constants (for aqueous solutions) yields a set of derived values for k_2. From these it can be seen that the quenching rate is approaching that predicted for diffusion-control ($k_2 = 3.3 \times$ $\times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ for iodoacetic acid $5.6 \times$ $\times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ for *p*-anisic acid).

The next task will be to differentiate between «static» and «dynamic» factors in each individual value of K_{SV}, i.e., effects due to ground-state complexing of U(VI) and those due to kinetic encounters of U(VI)* and quencher. This we propose to do by examining the accelerative effects of the added substrates upon the lifetime (and not just the intensity) of $(UO_2^{2+})^*$ by laser flash photolysis.

To summarise, the quenching of $(UO_2^{2+})^*$ by organic molecules is effected by a variety of pathways including exciplex formation with aromatic rings and isolated π-bonds, by heavy atom effects and by «chemical» quenching: the latter is associated in the case of alcohols by abstraction of a hydrogen atom from a hydroxylated carbon atom and a similar pathway may well operate with ethers, although this point remains to be settled.

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RESUMO

Estudam-se os mecanismos de desactivação do primeiro estado electrónico excitado do ião uranilo por moléculas orgânicas. As constantes cinéticas de sufocação do uranilo por álcoois, obtidas por medidas de luminescência e por fotólise por relâmpago, dependem da estrutura molecular e da substituição de átomos de hidrogénio por deutério. Estudos por r.p.e. sugerem que o processo de desactivação é devido à abstracção de átomos de hidrogénio por $(UO_2^{2+})^*$.

Apresentam-se também estudos cinéticos da reacção do uranilo excitado com ácidos carboxílicos, éteres, alcenos e halogenetos de alquilos. Os mecanismos da sufocação parecem ser de várias naturezas nomeadamente através de efeitos de átomos pesados, formação de exciplexos e devido a reacções químicas.

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CONCEPTS FOR PRETREATMENT-LAND APPLICATION FOR SMALL MUNICIPAL SYSTEMS (3)

The substitution of the plant-soil receiver system for the stream or water receiver requires a substantial alteration in objectives, waste and process characterization, design, and philosophy. From the environmental impact or waste capacity point of view these two alternatives receivers have very different characteristics. After reviewing some of these salient differences the authors will examine conventional secondary treatment in light of the limitations of land application as well as the potential for less complete pretreatment. Finally a discussion is included of the economic trade-offs encountered in land system design and the research needs to further optimize current municipal land application technology.

1 — INTRODUCTION

The stream or surface water receiver characterization begins with the level and nature of microbial populations. SINCLAIR [1] has evaluated the active biomass for stream systems as 10-50 mg/l with the predominant species being aerobic. The varietal microorganisms break down organic compounds as biomass is produced in a delicately balanced web. The magnitude of populations present in the stream liquid is not large thus small perturbations of nutrient levels, such as a slug of less treated municipal wastes, cause increased microbial levels which often have dramatic and adverse impact on this ecosystem. For stream systems the maintenance of aerobic conditions depends on oxygen transfer through the liquid phase beginning with the stream surface. Oxygen transport is then by molecular diffusion with the eddy action of the stream providing enhanced diffusion of 5 to 10 times the reaeration rate of stationary liquid systems. Measured self purification rate ($f = r/K$), the ratio of aeration rate (r) and deoxygenation (K), vary from 0.5-1 for small ponds and backwaters to above 5 for rapids and waterfalls [6].

Waste treatment for stream discharge must consider parameters such as color and suspended solids because of the use and nature of the nation's waterways. Color removal may be only for aesthetic reasons while organic suspended solids are removed to preclude settling out in regions of lower stream

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This paper was presented at the Transport processes section.

velocity. These parameters are focused on here simply for comparison to land receiver systems.

Characteristic residence times of streams in the 22 water resource regions of the United States is on the order of 2-8 days, with the residence times of the longest rivers ranging up to this is roughly the time available for waste stabilization. Thus the overall description of the stream system is a balanced microbial population of relatively low numbers which must be maintained not only for adequate waste stabilization but for aesthetic or public use goals.

The plant-soil receiver system is also a balanced microbial system but with natural populations of 8,000-10,000 mg biomass/l — some 200 to 800 times larger than the stream receiver. In fact, with normal application of waste the soil microbial populations often increase 50 to 100-fold above this level with no adverse effects. The purpose of the multifarious soil mantle species is to immobilize, mineralize, and microbially restructure compounds for incorporation into bacterial biomass or plant structure, for entry into the food chain. The tremendous adaptability of large mixed populations of microorganisms also allows for evolution of certain species to utilize compounds not ordinarily encountered in nature.

Another soil capability which is very limited in the stream system is absorption and adsorption of waste constituents. Soil sorption has the effect of greatly increasing system residence time to allow for slower degradative processes. This capability along with the physical filtering characteristic of soils leads however, to a potential disadvantage which is the very slow reversibility of toxic or adverse conditions which may occur. Thus, long term simultaneous monitoring and test studies are necessary with land application systems. In addition since this sorption capacity is finite unless removal mechanisms are available it will eventually deplete the soil capacity and require corrective measures.

Waste applied to soil need not have organic suspended solids, color, or turbidity removal since land usages and capabilities do not require it. Characteristic residence times for normal applications of soil water are 10-15 weeks through a 10 foot soil layer with the organic or solids residence times ranging up to years. The soil system is also predominantly aerobic but the oxygen transfer is enhanced by the dispersion of wastewater in and around soil particles. Thus oxygen migrates to soil depths by gas-gas diffusion and then into the thin liquid films for reaeration of wastewater. Such oxygenation is more rapid than diffusion through a similar depth of liquid even with liquid mixing. Overall, the plant-soil receiver is a large, balanced microbial population with soil particle sorption to aid in waste stabilization. It is quite tolerable

Table 1

***Distribution of selected domestic waste constituents from 1 MGD activated sludge plant* [2, 3]**

Parameter	Sludge effluent				Clarified effluent			
	Concentration [ppm of d.s.]	lbs per year	Nitrogen to parameter ratio	Land application rate* [lb/A/yr]	Concentration [mg/l]	lbs per year	Nitrogen to parameter ratio	Land application rate* [lb/A/yr]
Cu	900	630	55	9	.04	120	570	.9
B	30	23	1500	.33	.7	2000	33	15
Zn	2400	1700	20	24	.06	180	380	1.3
N	50,000	35,000	1	500	23	69,000	1	500
P	45,000	30,999	1.1	440	13	39,000	1.75	280
H_2O	65×10^6	4×10^6		$.58 \times 10^6$		2.7×10^9		20×10^6

* Based on applying at a rate which matches crop uptake of nitrogen (500 lb/A/yr) to land application.

Table 2

Effluent constituents of activated sludge plant and relation to plant-soil receiver system

Parameter	Sludge stream			Effluent stream		
	Approximate allowable land receiver rate [lb/A/yr]	Generation rate [lb/yr]	Needed acreage	Approximate allowable land receiver rate [lb/A/yr]	Generation rate [lb/yr]	Needed acreage
Cu	2	630	315	2	120	60
B	4-5	23	5	4-5	2000	400
Zn	5-10	1700	170-340	5-10	180	20-40
N	500	35,000	70	500	69,000	140
P	500	30,000	60	500	39,000	80
H_2O	80 A.in/A/yr	200 A.in/yr	2.5	80 A.in/A/yr	13,500 A.in/yr	170

of perturbations in waste loadings and has a large evolutionary capability.

2 — MUNICIPAL SYSTEMS

The conventional package plant treatment system usually produces two effluent streams, sludge or solids and clarified effluent. The distribution of the various waste constituents between these streams for a conventional activated sludge plant (Table 1) is an indication of treatment efficiencies for conservative and nonconservative elements, and is the basis for land application recommendations for these waste streams. In considering both streams separately with respect to the plant-soil receiver the concentrating effect of sludge removal and soluble carbon stabilization alters the ratio of the waste constituents. This may reestablish the particular constituent which controls or limits the number of pounds of sludge or effluent which are applied per acre per year.

To calculate limiting conditions, the acceptable land loading rate must be estimated and then divided into the generation rate of the constituent in each effluent stream to give the areal requirement. The constituent with the largest acreage requirement is limiting and thus serves as the basis for loading, Table 2. The nitrogen loading shown is designed to match the growing crop nitrogen uptake of about 500 lb/A/year for hay crops while the water rate for most moderately-to well-drained soils is 1.5 to 2 acre in per acre per week. The heavy metal areal loading rate is currently not well defined and varies over wide ranges in actual waste application practices. Thus the numbers and metals presented in Table 2 are representative of the low level of some current applications and are rates which have not manifested adverse effects. These rate usages should be coupled with monitoring of soils, soil water, and cover crop for toxic trends. Generally the heavy metal loadings shown are below many current sludge application rates but well above the rates at which crops would take up these heavy metals [7].

For the clarified effluent stream nitrogen and water are about equally limiting with the heavy metals requiring many fewer acres. For the sludge stream heavy metals are limiting with the corresponding nitrogen and phosphorus loadings being quite low. Small municipalities or housing developments often have no easy access to incineration or landfills so they must find land for both sludge and clarified effluent. Also because these two streams have quite different ratios of metals to nitrogen or metals to water it seems clear that one is really dealing with total effluent in two streams and that there may be cost advantages to not separating them or even to recombining them so that there is only one type of effluent handling system.

Table 3

Selected parameters of total activated sludge system effluent (1 MGD) and relation to plant-soil receiver

Parameter	Total system effluent					
	Concentration* [mg/l]	lb/year	Nitrogen: parameter ratio	Land application rate** [lb/A/yr]	Approximate allowable land receiver rate [lb/A/yr]	Needed acreage
Cu	.24	750	140	3.6	2	375
B	.70	2020	48	10	4-5	405
Zn	.60	1880	58	9	5-10	180-360
N	34	104,000	1	500	500	210
P	23	70,000	1.5	340	500	140
H_2O_5		14,000 A.in/yr		70	80 A.in/A/yr	175

* Obtained by summation of two streams in liquid volume of a million gallons.

** Based on applying at a rate which matches crop uptake of nitrogen (500 lb/A/yr) to land application.

The total effluent could be reduced by total recycle of sludge to further reduce the solids prior to a liquid land application system. Because all components listed in Table 2 except nitrogen are conservative in conventional treatment the total effluent will resemble the sum of the two effluent streams, sludge and clarified effluent, and also the raw waste input. The corresponding calculations for total effluent are given in Table 3 and one can see that heavy metals and then nitrogen are again limiting with the water limitation rate being much lower. Therefore if economics are favorable and unless there is a well defined, long term means of removing sludge from the total system, such as landfill or reuse processes, the total effluent must be considered in planning land application. In this

Table 4

Representative heavy metal and nitrogen losses in lagoon systems for swine waste [8, 9]

Unit	Loading rate	Copper			Zinc			Nitrogen		
	# COD/ft³/day ×10³	Influent [mg/l]	Effluent [mg/l]	% loss	Influent [mg/l]	Effluent [mg/l]	% loss	Total pounds loaded	Pounds accounted for	% loss
Two lagoon series										
First lagoon	58	6.6	.5	92	4.3	.3	93	—	—	—
Second lagoon		.5	.25	50	.3	.15	50	—	—	—
Pilot scale lagoon 7/10/73-10/21/74	58	—	—	—	—	—	—	295	95	68
Pilot scale lagoon with surface aeration	116	—	—	—	—	—	—	301	164	45

case cost savings could be expected for operations which treat by total recycle the waste input or for recombination of sludges and effluent to arrive at a single handling system for land application.

There is no net loss of conservative elements such as heavy metals within conventional extended aeration or activated sludge plants. Hence alternative processes not currently available will be needed if reduction in heavy metals levels are to occur. However, as nitrogen is also limiting in land application of total effluent the reductions through secondary treatment lead directly to a reduction in land requirements.

3 — PRETREATMENT

The use of processes which reduce nitrogen by some percentage of the inflow can be used if the savings in land costs are significant. This percent loss of nitrogen could be achieved by ammonia stripping or by denitrification of secondary effluent and would lead to a waste stream which balances heavy metal and nitrogen loads and is then limited by liquid application rates.

Lagons with surface aeration for odor control prior to land application provide a lower level of pretreatment. Heavy metal and nitrogen removals have not been well evaluated for municipal waste but if research with aerated-unaerated series animal waste lagoons is indicative, the lagoon offers several advantages. For a water-intensive swine unit the overall heavy metals reductions are 90 % for the first and second lagoons respectively in a series arrangement, Table 4. The nitrogen removal (excluding the amount settled in the sludge) is approximately 45-70 % with surface volatilization being the removal mechanism. Surface aeration turbulence can be used to augment these losses.

The sludge buildup for a predominantly degradable input such as municipal waste or swine waste is relatively slow with bottom sealing, compaction, and strong anaerobic activity occuring in the sludge zone. As future sludge levels fill these lagoons the possibility of water removal and filling the site with earth may be realistic or if extractive measures become available the heavy metals are present in concentrated form. The low capital and operational cost of lagoons and the heavy metal and nitrogen removal capability make these systems an excellent candidate for pretreatment prior to land application for small municipal type systems.

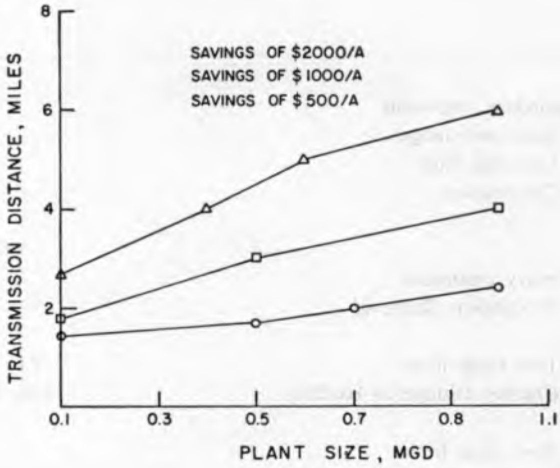

Fig. 1

Break-even pumping distance of various costs per acre of land can be achieved

4 — LAND TREATMENT ECONOMICS

Detailed system design for land application systems is not covered here, but one factor, control of aerosol drift, is mentioned as an example of current municipal waste adaptions. In order to minimize aerosol drift the use of low trajectory, 5° trajectory and maximum stream elevation of 1.5 ft above nozzle, and low pressure (50-60 psi) sprinklers are recommended. In addition the development of a meteorological control system is underway to prevent sprinkler application at wind velocities above specified limits. Further control of aerosol drift is achieved by the maintenance of a tree line at about 25-100 feet from the outer zone of liquid application. This is the mist zone and the area of maximum microbial drift. If trees are not available the transplanting of 20-25 ft high trees has been shown feasible [10]. It is not possible to specify the buffer zone beyond the tree line as the regulations and research data are not now available. The impact of large buffer zones is dramatic for small system costs and is discussed under system economics.

The cost of land application for small domestic

Table 5

Approximate costs for components of waste treatment and land application systems [4, 5]

		Capital costs [$/1000 gal]	Operating and maintenance [$/1000 gal]	Total annual costs [$/1000 gal]
Secondary treatment				
Activated sludge		.21	.14	.35
Trickling filter		.19	.10	.29
Chlorination		.006	.015	.021
	Effluent			
Tertiary treatment				
Phosphorus Removal				
Two stage lime Clarifier (sludge to landfill)	.5-1 (mg PO_4 — P/l)	.09	.07	.16
Two stage lime Clarifier with tertiary filter	< .1 (mg PO_4 — P/l)	.16	.14	.30
Nitrogen removal				
Ammonia stripping	~ 2 mg NH_3/l	.071	.016	.087
Dispersed floc Nitrification-denitrification	~ 2 mg NO_3/l	.15	.24	39
Land application (w. o. transmission to site or land costs)		.050	.10	.15
With land $1000/A (w. o. transmission)		.070	.10	.17
With land $2000/A (w. o. transmission)		.090	.10	.19

systems has been well documented [4, 5], Table 5. The use of land application as a substitute to tertiary treatment for nitrogen, phosphorus, color, and solids removal to meet current regulations certainly is less expensive, Table 5. Of course, simply attaching the land application to existing facilities leads to some uneconomical situations especially because of land costs and availability. However experience indicates that with consideration of pumping greater distances and with relocating new sites, land application can be made less costly than even the less stringent tertiary treatment processes. The cost savings by pumping to areas of lower land cost is illustrated in fig. 1. Artificially large buffer zones, Table 6, have the maximum adverse effect on small systems for which alternative tertiary treatment processes are prohibitive both from the capital and operational viewpoint. Experiences in the United States point to and current research is underway to verify the use of 100-150 foot buffer zones.

In terms of operating and maintenance costs land application is lower in comparison to tertiary or even secondary treatment such as the activated sludge process. Additionally the simplicity of operation and hence the continued successful operation of land application systems are much more favorable than tertiary treatment. In the operational and maintenance costs for land systems labor is low (as little as 1 man year for 1 MGD) with electricity being the major cost [4].

One point which is often overlooked in system design is the economic trade-offs available because emphasis is often placed on handling or applying what comes from the plant. The high cost of barrier zones, Table 6, especially for the small domestic system (.05, .1 and .5 mgd) directs consideration of alternative ways of reducing this cost. Greater level of pathogen kill in-plant would lead to less need for large buffer zones beyond the 75-100 foot mist zone. This large savings can go into chlorination which is relatively inexpensive, Table 5 hence a net savings can be realized by trading off in-plant treatment for large buffer zones.

Table 6

Acreage requirements and land costs for various barrier distances [4]

Treatment scale (MGD)	Barrier distance in feet			
	0	100	300	500
	(land requirement — acres) (1)			
.05	9	16	34	60
.10	18	26	50	81
.50	89	108	152	203
1.0	175	201	260	325
10.0	1750	1831	1999	2174
	(cents per thousand gallons per $1,000/acre for land) (2)			
.05	3.86	6.89	15.19	26.71
.10	3.86	5.83	11.04	17.86
.5	3.86	4.78	6.71	8.96
1.0	3.86	4.44	5.73	7.18
10.0	3.86	4.04	4.41	4.80

(1) Based on 1.5 acre inches per week.

(2) Based on 30-year life of land facility, no salvage value, 7 percent discount rate.

5 — RESEARCH NEEDS AND SUMMARY

The use of land application is not without problems especially as it is commonly used as an add-on to conventional treatment. Research thus should focus on reducing the current problems associated with application methods and also seek to optimize the pretreatment of municipal waste to allow total effluent land application. The first research need is an irrigation optimization scheme for control of droplet size to minimize drift. Application systems such as gated pipe, trickle or drip procedures, furrow system, and other means of placing waste on large areas to minimize aerosol drift and cost should be investigated. Research is needed in the selection of specific crops which under the conditions of a land application system would yield the maximum profit. Emphasis should be directed to water tolerant high cash value crops. The effective use of land forming and drainage to improve sites for better agricultural use of application sites would also lead to more cash crop production.

Within the treatment strategy for domestic wastes, research should emphasize the removal of heavy metals separate from the large volume of organic matter associated with sludge. This would allow the organic solids to go to the plant-soil receiver which can easily handle a broad range of carbon loading rates. Secondly, sterilization or pathogen control without extensive aerobic treatment should be given high priority. The stabilization of organic matter is best done in the plant soil system so elimination of pathogens in raw waste would lead to a more optimal system.

In summary, the use of land application for small domestic systems is entirely feasible and the trend of regulations pursuant to the zero discharge regulations further emphasizes the cost advantages of land application coupled with land use planning. The question no longer is whether it is feasible but how do we design the least cost land based system. The engineering challenge is now to reduce the entire system cost and arrive at an optimal system which actually takes into account the plant-soil receiver system capabilities and limitations within the changing constraints of environmental and public health guidelines.

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RESUMO

A substituição de um sistema de depósito tipo lamaçal pelo de água ou corrente implica uma alteração substancial de objectivos, caracterização do processo e resíduos, projecto e filosofia. Do ponto de vista do impacte ambiental ou de capacidade em resíduos, estes depósitos alternativos têm características muito diversas. Após revisão de algumas das principais diferenças, examina-se o tratamento secundário convencional à luz das limitações de utilização das «terras», bem como o potencial para um pré-tratamento menos complexo. Finalmente, apresenta-se uma discussão dos aspectos económicos encontrados no projecto de sistemas de detritos e da investigação necessária à contínua optimização da tecnologia de utilização de detritos municipais.