

TEMPERATURE EFFECT ON WHEY PROTEIN FOULING

EFECTO DE LA TEMPERATURA SOBRE LAS PROTEÍNAS DE LACTOSUERO

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Resumen

El presente trabajo es un estudio del fenómeno de incrustación de la proteína del suero de leche al interior de un intercambiador de calor por donde fluye agua caliente por entre los dos tubos. La cinética de incrustación depende de los efectos de la transferencia de masa, que es una función de la solubilidad de las proteínas. Para describir la cinética de incrustación de las proteínas se desarrolló un algoritmo de cálculo dependiente de la solubilidad. La solubilidad de la proteína fue determinada en una investigación por separado. Los resultados mostraron que el tiempo necesario para que el tubo de radio interior disminuyera en un 30% de la radio original fue menor para altas temperaturas. Además, la deposición de las proteínas de suero de leche fue más intensa en la entrada que en la salida. Por lo tanto, la tasa de reducción de radio fue más rápida en esa zona. El experimento para comprobar el algoritmo se llevó a cabo en una planta piloto.

Palabras clave: suero de leche, proteínas, Temperatura, incrustaciones, solubilidad.

Abstract

In the present work, whey protein fouling phenomenon was studied, when flowed in the inner tube of a double tube heated by hot water which flows in the ring space between them. The fouling kinetics depends on the mass transfer effects, which is a function of protein solubility. To describe the fouling kinetics a calculus algorithm was developed, having as subsidy the protein solubility itself. The proteins solubility were determined in a separate investigation. Results showed that the time necessary for the tube's inner radius to decrease in 30% of the original radius was smaller for high temperatures. Besides, whey protein deposition was greater at the tube's entrance than in its exit. Therefore, the rate of radius reduction was faster in that area. The experimental check for the algorithm was conducted in a pilot plant.

Keywords: whey, protein, temperature, fouling, solubility.

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Introduction

Milk is a complex mixture, constituted by a composed emulsion of fat and a colloidal protein dispersion, with lactose solution. Such constituents are complemented by minerals (mainly calcium), vitamins, enzymes and organic composites (Kon, 1972, Torii et al, 2004, Magalhães and Telmo, 2006).

When used for commercialization, milk becomes a product greatly perishable, that is, its liquid state and its nutritional composition becomes it susceptible for microorganisms proliferation, as those originally in milk or that introduced by manipulation (Martins *et al*, 2007).

For that reason, since 1966 the pasteurization became mandatory in dairy products. However, an important problem in pasteurization is the fouling, implicating in the reduction of processing efficiency, in the bombs overloading, in periodic machine stopping for cleaning and even its substitution. Due to those reasons, it is reasonable that the heat exchangers efficiency can be evaluated recognizing the situations that raise its efficiency losses, and the detection and quantification of fouling deposits in the wall is one of the techniques for evaluation of the heat exchangers performance (Veisseyre, 1972; Afgan and Carvalho, 1998).

Fouling is an important problem in many heat exchangers, that requires careful monitoring. In spite of precautions taken in the design of the heat exchanger, fouling is an unavoidable problem, that can involve the equipment thermal performance reduction, the pump overcharge, the periodical stop engine for cleaning and the heat exchanger replacement (Belmar *et al*, 1993, Afgan and Carvalho, 1998, Pelegri and Gasparetto, 2004).

Fouling in food industry is a severe problem compared with other industries. For example, while in the petrochemical refineries, heat exchangers may only be cleaned annually, in the dairy industry it is common practice to clean every 5-10 hours. In the food industry where biological fluids are heated, fouling may be a particularly serious problem (Murray & Deshares, 2000).

The problem manifests itself economically through loss of efficiency of the heat exchanger, in time and materials required to clean fouled surfaces, in loss of product, and through losses of vitamins, minerals, and other nutrients in the foul layer. Besides, the fouled material joined the wall allows microorganisms adhesion. The fouling phenomenon is the consequence of protein deposition, which was previously denatured and joined in the hottest areas of the heat exchangers surface. When the temperature of the protein solution is raised high enough for a given time, the protein is denatured. Proteins are denatured by the effect of temperature on the non-covalent bonds involved in stabilization of secondary and tertiary structure, for example, hydrophobic, electrostatics and hydrogen bindings (Petermeier et al, 2002). When the protein secondary and tertiary structures of a protein are unfolded, the hydrophobic groups interact, and reduce water binding. Such hydrophobic interactions lead to aggregations, followed by coagulation and precipitation (Vojdani, 1996). In other words, denaturation decreases protein

solubility compared to native protein, and leads to aggregation and difficulty of reversal upon cooling, resulting in its fouling or mechanical deposition, that is also considered as a fouling form.

Milk fouling deposits consist of a layer of protein aggregate and minerals which can be several millimeters thick. Deposits formed at temperatures below 110 Celsius degrees contain approximately 50-60% protein and 30-35% minerals. Half of the protein deposit is β -lactoglobulin. Below about 70 Celsius degrees β -lactoglobulin forms an adsorption layer on the heat transfer surface of less than 5 mg/m²; however, on heating above 65 Celsius degrees, it becomes thermally unstable. Two types of reaction occur sequentially. The protein first partially unfolds, in molecular denaturation, exposing reactive sulphhydryl (-SH) groups, and then polymerises in intermolecular aggregation, either with other β -lactoglobulin molecules or with other proteins such as β -lactalbumin (Belmar et al, 1993, Belmar & Fryer, 1998).

Experimental Procedure

Mathematical model: To develop a mathematical approach for fouling, it was considered the double circular tube in figure 1, where R_0 is the inner radius, and L is the length of the tube.

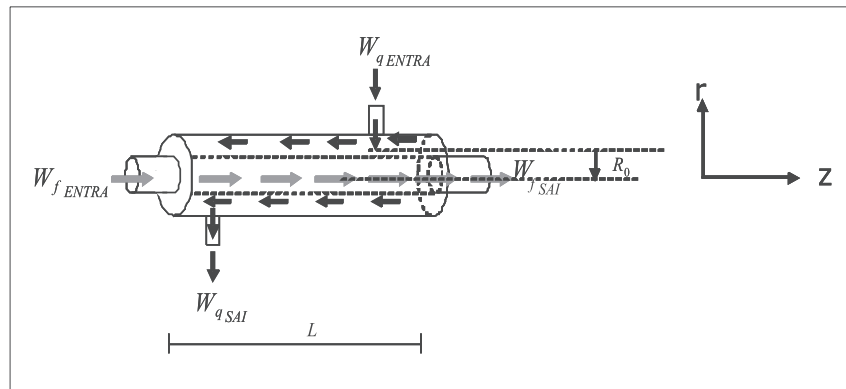


Figure 1: Double circular tube heat exchanger

Milk flows with a W_f flow rate and T_{f0} initial temperature. Water drains in the annular space between the two tubes, in the same direction of the white egg, with W_q flow rate and T_{q0} initial temperature. The algorithm was developed for cylindrical pipes because this geometry allows a simpler mathematical model due to its symmetry.

Sandu and Lund (1982) developed a numerical procedure for fouling dynamics, relating the mass balance with time for constant Z and with Z for constant time. The simplifying assumptions were introduced: (a) the processed fluid is a binary system of β -lactoglobulin (A species) in milk (B species), where only A species is fouling; (b) the deposition is a process that occurs at low mass transfer rates; (c) no production of species A in the bulk of the processed fluid occurs; (d) the mass flow rate of the processed fluid is maintained constant

during the heat process, that is, $W_f = \text{const.}$; (e) the fluid is incompressible; (f) the removal process can be entirely neglected.

Using the cylindrical coordinates of the fouling system depicted in Fig.1, it is more convenient to define the local coordinate of the liquid-solid interface by R , where $R = f(Z, t)$. The local coordinate of the solid-liquid interface, R , may take values between R_0 at time zero, and 0, at the time when the tube plugs. A numerical procedure was developed to resolve the differential equations, relating the mass balance with time for a constant position Z . At a given time $t = \text{const.}$, a mass balance equation for an infinitesimal cylinder of length dZ can be written, when the decrease of average bulk concentration of the processed fluid is the result of the mass transport along the surface of the cylinder. The elementary cylinder is located at the distance Z , and has a constant radius $R = f(Z)$. The mass balance equation has resulted in:

$$d\bar{C}_A = \frac{2\pi}{W_f \xi} \left\{ p k_{xA} (\bar{C}_A - C_{A0}^*) \right\} R dZ \quad (3)$$

where:

W_f = mass flow rate [Kg/s]; average bulk concentration [Kmol/m³]; C_{A0}^* = local saturation concentration at the liquid-solid interface [Kmol/m³]; ξ = molar density of the binary system [Kmol/m³]; p = local average bulk density [Kg/m³]; dZ = tube length [m]; k_{xA} = mass transfer coefficient of species A [Kmol/m².s].

The only boundary condition needed is: at $z = 0 \rightarrow \bar{C}_A = \bar{C}_{A0}$, and the local saturation concentration was calculated, through the β -lactoglobulin solubility curve, determined in this work. At a distance $Z = \text{const.}$, a local mass balance equation for an infinitesimal cylinder of length dZ can be written, where its thickness, dR , is the result of the mass transport during the time dt :

$$-dR = \frac{M_A}{\xi \rho_A} k_{xA} (\bar{C}_A - C_{A0}^*) dt \quad (4)$$

where:

M_A = molecular weight of A species [Kg/Kmol]; ρ_A = average density of fouled layer [Kg/m³]. k_{xA} in equations 2 and 3 is the local mass transfer coefficient of species A, and is referenced to the liquid-solid interface coordinate R . It can be calculated after the average velocity, temperature and concentration profiles are known. The average velocity was calculated by the continuity equation.

$$\bar{V}_Z = \frac{W_f}{\rho \cdot \pi \cdot r^2} \quad (5)$$

where:

\bar{V}_Z = average velocity at Z direction [m/s]; mass flow rate [Kg/s]; fluid density [Kmol/m³]; tube radius [m].

Obviously, the next step is to find the Z-dependence of the local, average bulk temperature of the processed fluid, T_f . Usually, the fluids temperature in a heat exchanger are not constant but they vary through its length, as the heat drains form the hot to the cold fluid. The changes in the fluids temperature can be illustrated in fig. 2.

In this way, a heat balance equation for the infinitesimal cylinder in figure 2 can be written, at constant time, when the increase of the temperature of the processed fluid, dT_{zf} , is the result of the heat transport through the surface of the cylinder. For parallel currents heat exchanger, showed in fig. 2, the heat transferred through an infinitesimal area element can be written:

$$dq_z = -W_f \cdot cp_f \cdot dT_{zf} = W_q \cdot cp_q \cdot dT_{zq} \quad (6)$$

where:

dq_z =heat transferred into the infinitesimal area, at z direction [W/m²]; infinitesimal area [m²]; W = heat and cold fluid mass flow rate [Kg/s]; fluid specific heat [J/Kg.°C]; dT_{zf} =cold fluid temperature variation [°C]; dT_{zq} =hot fluid temperature variation [°C].

Integrating equation (6) and then rearranging it, the heat transfer rate can be written as:

$$q_z = -W_f \cdot cp_f \cdot (T_f - T_{f0}) = W_q \cdot cp_q \cdot (T_q - T_{q0}) \quad (7)$$

The heat transferred in the axial direction also can be written as:

$$dq_z = U \cdot (T_q - T_f) \cdot dA \quad (8)$$

where:

U =overall heat transfer coefficient [W/m².°C]; dA infinitesimal area [m²]; T_q =hot fluid temperature [°C]; T_f =cold fluid temperature [°C].

Solving the system composed by equations 6 and 8, it is obtained the following fluid temperature profiles:

$$T_f = T_{f0} + \frac{dq}{W_f \cdot cp_f} \quad (9)$$

$$T_q - T_{q0} = T_f - T_{f0} + (T_{q0} - T_{f0}) * \left(-U \cdot \left(\frac{1}{W_q \cdot cp_q} + \frac{1}{W_f \cdot cp_f} \right) \cdot dA \right) \quad (10)$$

Replacing equation (7) in (10), the global heat transfer rate can be written as:

$$q_z = -(T_{q0} - T_{f0}) U \cdot dA \quad (11)$$

The internal and external surface temperatures were calculated through the energy balance in the two surfaces, resulting in:

$$\frac{T_f - T_p}{R_i} = \frac{T_p - T_{pe}}{R_m} = \frac{T_{pe} - T_q}{R_e} \quad (12)$$

where:

T_p =internal surface temperature [$^{\circ}\text{C}$]; T_{pe} =external surface temperature [$^{\circ}\text{C}$]; R_i =tube internal thermal resistance [$\text{W}/^{\circ}\text{C}$] $^{-1}$; R_e =tube external thermal resistance [$\text{W}/^{\circ}\text{C}$] $^{-1}$; R_m =thermal resistance of the heat exchanger material [$\text{W}/^{\circ}\text{C}$] $^{-1}$.

The overall heat transfer coefficient (U) was computed by the next equation:

$$U = \frac{1}{\frac{1}{h_i} + \frac{A_i \cdot \ln\left(\frac{r_e}{r_i}\right)}{2 \cdot \pi \cdot k_m \cdot L} + \frac{A_i}{A_e} \cdot \frac{1}{h_e} + \frac{A_i \cdot \ln\left(\frac{r_c}{r_f}\right)}{2 \cdot \pi \cdot k_f \cdot L}} \quad (13)$$

where:

U = overall heat transfer coefficient [$\text{W}/\text{m}^2 \cdot ^{\circ}\text{C}$]; h_i = internal surface convection heat transfer coefficient [$\text{W}/\text{m}^2 \cdot ^{\circ}\text{C}$]; h_e = external surface convection heat transfer coefficient [$\text{W}/\text{m}^2 \cdot ^{\circ}\text{C}$]; A_i = internal surface area [m^2]; A_e =external area [m^2]; r_e =double pipe heat exchanger radius [m]; r_i = inner tube radius [m]; r_c = clean inner tube radius [m]; r_f =fouled inner tube radius [m]; L = infinitesimal tube length [m]; k_m = heat exchanger material thermal conductivity [$\text{W}/\text{m} \cdot ^{\circ}\text{C}$]; k_f =fouled layer thermal conductivity [$\text{W}/\text{m} \cdot ^{\circ}\text{C}$].

The internal and external convection heat transfer coefficients were computed by Nusselt number (Incropera & Witt, 1998).

From Chilton-Colburn analogy between heat and mass transfer, it was obtained:

$$\frac{k_{xA}}{\xi v_z} \left(\frac{\mu_{ap}}{\rho D_{AB}} \right)^{2/3} = \frac{h}{\rho C_p v_z} \left(\frac{C_p \mu_{ap}}{k_f} \right)^{2/3} \quad (14)$$

where:

h =convection heat transfer coefficient [$\text{W}/\text{m} \cdot ^{\circ}\text{C}$]; C_p = specific heat [$\text{J}/\text{Kg} \cdot ^{\circ}\text{C}$]; diffusivity [m^2/s]; D_{AB} = thermal conductivity of fouled layer [$\text{W}/\text{m} \cdot ^{\circ}\text{C}$].

Equation (14) provides kxA parameter of equations (3) and (4). A general solution to fouling dynamics, involving equations (3) and (4) is possible only by numerical procedures. The strategy of a numerical procedure is explained on the basis of figure 3. The assumption

is made that the deposition does not have an angular dependence, but only a time and Z dependence. At a given time, $t = \text{const}$, and at a distance Z_i from the entrance of the tube, the coordinate of the liquid-solid interface is R_i . Defining this as point i , when $t = \text{const}$ and using the local conditions at the point i , when $t = \text{const}$, it can be made the following calculations:

a) From equation (3), the decrease of average bulk concentration from point i to point $i+1$ when t is constant:

$$\Delta \bar{C}_{Ai} = \frac{2\pi}{W_f \cdot \xi_i} \left[\bar{\rho}_i k_{x, Ai} (\bar{C}_{Ai} - C_{A0i}) \right] R_i \cdot \Delta Z \quad (15)$$

where ΔZ is the distance between the point i and the point $i + 1$.

b) The variation of the coordinate of the liquid-solid interface from point i to the point $i+1$, when $t = \text{const} + \Delta t$:

$$\Delta R_i = - \left(\frac{M_A}{\xi_i \cdot \rho_A} \right) k_{x, Ai} (\bar{C}_{Ai} - C_{A0i}) \Delta t \quad (16)$$

where Δt is a given interval of time.

Based on the above equations, a numerical calculation can be developed, the calculation was developed, starting with $t=0$, when the surface is clean, and ending at a limiting value R of the coordinate liquid-solid interface. In this work, the running program was interrupted when the tube radius decreased in 30% of the initial value, or when reaching the maximum time of 100000 seconds. The program was developed in Delphi 2006 language which gave the R variation, in function of Z and t . However, a great amount of difficulty in running the computational program is introduced by the subroutines designed to calculate the profiles of velocity, temperature and concentration. Once these profiles are known, in the cross section of interest, the corresponding transfer coefficients can be computed.

The physical properties of the white egg and milk introduced in the program are in table 1.

- **Heat exchanger data:** The heat exchanger used in this simulation was a concentric double tube with parallel currents, where milk and white egg flows inside the inner tube at 40, 50, 60 and 70°C (T_{f0}) and Reynolds number of 10000. The water flows into the space among the two tubes at 83°C (T_{q0}) and Reynolds around 20000. Note that $T_f = f(T_q)$, but $T_{f0} \neq f(T_{q0})$. The tube is inox steel 304 and its dimensions are summarized in table 2.

The inner radius variation along the tube was calculated by finite differences method, where the length of the infinitesimal cylinder was 0.05m. In other words, a tube of 1.0 m length was fragmented in 20 infinitesimal tubes.

- **Fouling rig and operation:** The apparatus schematic diagram is shown in Fig.3. The heat exchanger used consists of a tubular heat exchanger, constructed in Food Engineering Laboratory, in Agronomy Science Department, according to project considered for Belmar et al (1993), represented in figure 3.

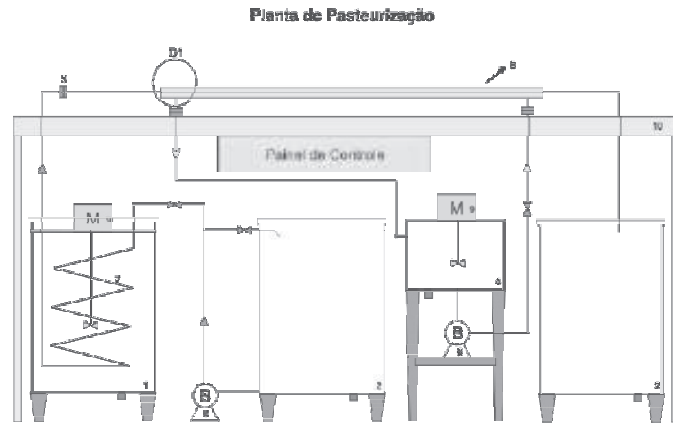


Figure 3: Pasteurization plant

Figure 4 represents the heat exchanger set up in the laboratory



Figure 4: Tubular heat exchanger

The pre heater consisted of a 30 m coil of $\frac{1}{2}$ pol. copper tubing mounted in a large drum filled with water. Temperature was regulated with an external controller. In heater section a thermal oil was used to provide hot fluid for the countercurrent heat exchanger. A high oil flow rate of 50 liters/min was used to maximize the heat transfer coefficient from the oil to the tube. The milk and oil inlet and outlet temperatures were measured by thermocouples, placed in entrance and exit heat section. Raw milk was received in a tank where it was pumped to preheating section and, after finished the process, the pasteurized milk was collected in another steel tank . Prior to fouling, the stainless steel tubes were cleaned for 30 minutes

at 45 Celsius degrees with a 1% (v/v) detergent to remove any oil deposit on the surface resulting from the manufacture. Milk was passed through the pre heater to ensure correct inlet temperature.

At the end of a run, the fouled tube was removed and carefully cut into 5 cm lengths, using a pair of scissors. Test sections were dried overnight and then weighed. Continually, the fouled deposition was removed from the tube wall and the cleaned tube was weighed. The fouling results were expressed in terms of protein grams per unit area.

Results and Discussion

- **Product Characterization:** The product lot used to calculate the protein solubility presented the whey centesimal composition characteristic, and the results are summarized in table 1.

Table 1: Centesimal composition of ALACENTM 895

ANALYSES	CONTENT (G/100G)
Moisture	4.940
Total Lipids	0.279
Ashes	3.540
Protein	80.33

- **Solubility Values:** The fouling table shows the protein solubility average values of two replicates, for the ALACENTM 895. The values present in that tables were calculated from equation (1). The values of the whey proteins solubility are illustrated in fig. 2.

Table 2: Protein solubility values of whey proteins

$T_0(^{\circ}\text{C})$	$P(\text{g})$	$\psi(\text{g/ml})$	$P.S(\%)$
40	1.015	0.0109	100.00
50	1.026	0.0088	86.39
60	1.0020	0.0068	67.91
70	1.020	0.0079	77.35
80	1.026	0.0075	74.46
90	1.0041	0.0034	33.57

From table 2 it could observe that the solubility decreased with the temperature due to the effect of the temperature in the bonds involved in the secondary and tertiary structures stabilization, where its unfolding favors the interaction among the hydrophobic groups, reducing the protein-

water interactions, indicating that the thermal protein denaturation occurred. But the protein solubility increased with the temperature where temperature increased from 60°C to 70°C, indicating that there was not coagulation nor aggregation between the protein molecules, possibly because the β -lactoglobulin is a dimer that is dissociated in monomers at 60°C and only above 70°C the proteins unfold and the hydrophobic groups react.

- **Simulation graphs:** The deposition of whey proteins was greater at the entrance of the tube than in its exit. Therefore, the radius reduction occurred faster in the entrance of the tube, that was the area chosen to make a comparative analysis of fouling of the proteins. Figures 5 and 6 present results of the radius reduction along the tube, when milk flows at several temperatures.

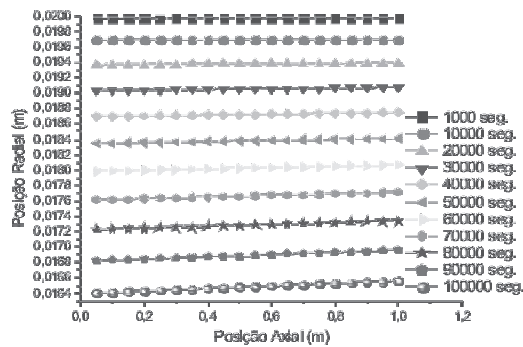
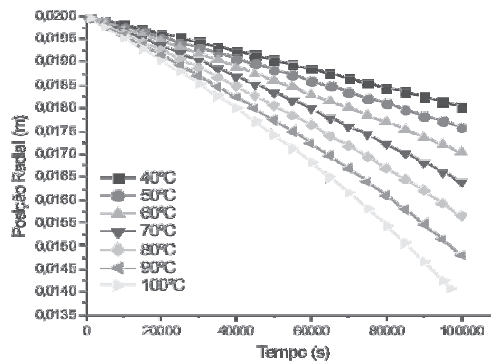


Figure 6: Internal diameter reduction due to laminar milk flow at 70°C

Figure 7: Internal diameter reduction with time, entry region, due to incrustation of β -lactoglobulin, laminar flow at pH 6,8



In figs. 5, it can be observed that, in the beginning, the radius didn't vary with Z coordinate; however, after some time, an inclination was observed in the straight line, that was growing along the time. Those results confirm the postulate that the fouling do not take place at constant rate, but accelerates with time. Results have also indicated that in the inlet region the deposition was more intense than in the outlet, because the diameter decreased more quickly in that area. As reduction of tube diameter was faster in its inlet, this will be illustrated in this area. From fig. 6 it also could be noted that inclination of the straight line is more accentuated for higher temperature entrance, indicating that fouling near the tube entrance is more intense for higher liquid inlet temperature.

- **Experimental data:** Experiments were conducted in which milk outlet temperature varied from 70 to 90 Celsius, for a constant Reynolds number of 1800 and a tube length of 1.8 m. The results are represented in Figure 7 showing that the total amount of deposition increases with milk outlet temperature. At 70°C, although the fouling is at low level in the inlet region, it increases significantly at some point down the tube, indicating that, for this temperature the fouling process may be reaction controlled.

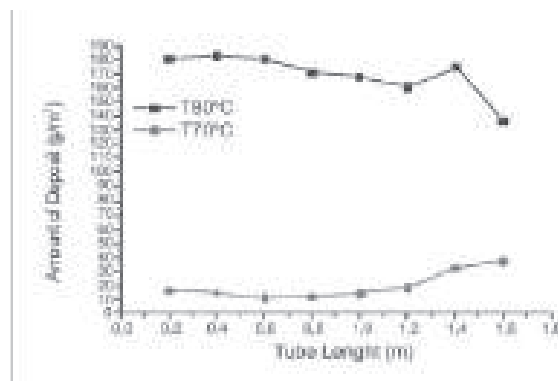


Figure 8: The effect of milk temperature on whey protein fouling

At 80°C the deposition was more accentuated in the inlet area than in outlet. These results confirm Pelegrine and Gasparetto (2004) observations, indicating that, in this temperature, the fouling process may be mass transfer controlled.

Figure 8 shows that experiments under the conditions described above produced significant increase in fouling as milk temperature is higher. Consequently, the fouling is faster when milk temperature is higher.

The fouling process also could be noted with mass flow rate decreasing, during milk processing. At 70°C the mass flow decreased along milk processing, from 0.00974 to 0.0062 Kg/s (36% reduction in mass flow rate). At 80°C this decrease was 47%, along the pasteurization process.

Conclusion

- About whey protein fouling analysis, it can be concluded that the process doesn't happen at a constant rate, accelerating with time, and in the tube inlet the deposition was more accentuated than in the outlet, because the radius reduction was more quickly in that area. Besides, the amount of the deposit in areas near the tube entrance was larger when the inlet temperature was higher, because the necessary time for the tube radius decrease in 30% was smaller when the fluid average temperature was higher. The algorithm here developed can be applied to foresee the protein deposition when food fluids flow inside a tube, being this an useful program in the controlling and automation in tubular heat exchangers.

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