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Boiling point and specific heat of meat extract

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ABSTRACT

Meat extract is a by-product obtained from the cooking broth of meat processing, which is used as a flavoring agent in cooking and in pharmaceutical products. Information on processing technology of meat extract and its corresponding thermodynamic properties have been seldom reported, making difficult the design of heat transfer processes with accuracy. Thus, the present work aimed to evaluate the boiling point elevation and specific heat of meat extract in the range of concentrations and temperatures found during its processing. Boiling point temperature was determined experimentally as a function of pressure and soluble solid concentration of meat extract. Different correlations based on Dühring’s rule, Antoine equation and the model proposed by Crapiste and Lozano were obtained to represent boiling point temperature and/or boiling point elevation in some processing conditions, resulting in good fitting accuracy. The representation of the experimental values of specific heat was evaluated by four empirical equations. The best fitting was acquired by using a quadratic model simultaneously dependent on concentration and temperature of meat extract. The close agreement between experimental and predicted values reinforces the applicability of the resulting models for designing evaporation systems.

Keywords: boiling point elevation, specific heat, Dühring’s rule, Antoine equation, heat transfer, multiple effect evaporators.

INTRODUCTION

Among the meat producing countries, Brazil is one of the most important, with 8 millions of tons produced annually [1], being the major exporter of concentrated meat extract. The meat extract is a by-product obtained from the cooking broth of meat processing, with yield production of 0.03 kg/kg of meat [2]. This product is rich in iron, proteins and amino acids, besides being object of great demand by the pharmaceutical and food industries around the world [3].

Technically, the production of meat extract involves two or more unit operations. An example of meat extract process can be observed schematically in Figure 1. Initially, the cooking meat by-product (meat juice) with 1.5 °Brix is subjected to a sterilization step, at 121°C during 3 min, in a plate heat exchanger fitted with a holding tube (Figure 1a). The concentration is carried out in a three-effect evaporation system, in which the meat juice is concentrated to 20 °Brix in the first effect, subsequently to 40 °Brix in the second effect, and finally up to 60 °Brix. The three evaporators can be used in direct flow or in counter-current flow arrangement (Figure 1b). As soon as finished the evaporation process, the meat extract is concentrated to 80 °Brix in a discontinuous process using a vacuum boiler.

The exposure of foodstuffs, such as meat extract, to high temperatures for long time periods potentially causes changes in the color and flavor of the material, which, in some cases can be acceptable or undesirable [4,5]. According to Bai et al. [6] the relatively low evaporation temperatures that prevail in vacuum evaporation imply that reasonable temperature differences can be maintained between the saturated steam used as heating medium and the boiling liquid, while using relatively low steam pressures. These operating conditions limit undesirable changes in the color and flavor of the product [7,8]. For aqueous liquids, the relationship between pressure and evaporation temperature may be obtained from thermodynamic tables or through theoretical and empirical relationships that correlate vapor pressure and temperature [5].

Although some physical and rheological properties of meat extract have been reported [9], the boiling-point elevation (BPE) and the specific heat (c_p) are needed properties in processes involving evaporation and heating. BPE describes the rise in boiling point of an aqueous solution as the soluble solid concentration increases, meaning that a solution with high concentration has a higher boiling point than one with low concentration. Some data on BPE, as for coffee extract [10] and blackberry juice [11], have been reported as a function of the water content and pressure.

Considering the importance of data on thermodynamic properties of meat extract and the lack of published information on these values, the present work aimed to evaluate the boiling point temperature, boiling point elevation and specific heat of meat extract in the range of concentrations, pressure and/or temperatures found during its processing.

MATERIAL AND METHODS

Raw material and sample preparation

Concentrated meat extract with 80 °Brix was obtained from the meat processing industry JBS–Friboi (Barretos, São Paulo, Brazil). The raw material was determined by Polachini et al. [9], where it was found 15.9% of water, 64.4% of protein, 19.1% of ash and 0.6% of fat. For experimental procedures, concentrated meat extract was mixed with distilled water and stirred for 10 min, resulting in fourteen samples with soluble solid concentration ranging from 1 to 60 °Brix.

Experimental procedures and mathematical analysis

Boiling point elevation: Boiling point elevation of the meat extract samples was measured using an apparatus similar to that presented by Moresi and Spinosi [12] as shown in Figure 2. The apparatus is composed of a glass flat bottom flask (F) with three openings. Each sample (approx. 180 mL) was introduced into the flask by means of tube A and heated by an electric heater provided with a magnetic stirrer model TE-0852 (Tecnal, São Paulo, Brazil). Once reached the boiling temperature, the sample was recirculated between tubes B and C. The liquid-vapor mixture released from the liquid surface flowed up through tube B, thus heating the thermocouple installed in the well, which was connected to a temperature transmitter model TT302 (SMAR, Sertãozinho, Brazil). Liquid particles were trapped in compartment D and returned to flask F, allowing vapor to enter reflux condenser R. Condensed vapor also returned to flask F through tube C, being controlled by the flow rate in valve V to keep the extract concentration constant.

A vacuum pump in the condenser allowed pressure to vary in the range of 5.8×10^3 to 9.4×10^4 Pa (abs.), being measured by differential pressure transmitters model LD-301 (SMAR, Sertãozinho, SP, Brazil) in two different positions in the vacuum tube. Static pressure data were collected using a data acquisition system with accuracy of 0.1 Pa. In each experiment, the cooling water flow was initiated in the reflux condenser, the vacuum pump was turned on with a valve regulated to provide a pressure of about 6×10^3 Pa (abs.), and the fluid was mixed and heated slowly. Temperature and pressure were then continuously recorded, and final values of boiling point associated with the pressure were registered after readings had been constant for at least 5 minutes. The procedure was repeated almost up to atmospheric pressure and allowed the measurement of boiling points at different pressures with the same extract concentration. Sample concentration was checked periodically and when the desired concentration was not reached, the procedure was repeated. The apparatus was calibrated according to Telis-Romero et al. [10] and Gabas et al. [11], using NaOH and LiCl as standard solutions in different concentrations. The measured values were compared with those presented by Perry and Chilton [13]. No significant differences were observed between the theoretical and experimental values at 95% confidence interval.

The experimental data of boiling point for each extract concentration were correlated with the boiling point of pure water at the same pressure through the Dühring's rule [14], expressed by Equation (1).

$$T_A = m_0 + m_1 T_{A0} \tag{1}$$

where T_A and T_{A0} are the boiling point temperature (K) of meat extract and the boiling point temperature (K) of pure water, at the same pressure, respectively; m_0 and m_1 are the model parameters. Values of T_{A0} were calculated by the Antoine equation (Equation 2) using the constants for water: A=18.3036; B= 3816.44 and C=-46.13 [13]:

$$\ln\left(P\right) = A - \frac{B}{\left(T_A + C\right)} \tag{2}$$

where P (mmHg) is the experimental pressure corresponding to T_A. Using the experimental data of T_A in Equation (2) it was also possible to correlate the boiling point temperature of meat extract with absolute vapor pressure, obtaining values of the Antoine constants A, B, and C, for each extract concentration. Moreover, it was possible to represent the elevation of boiling point of meat extract by an empirical model proposed by Crapiste and Lozano [15], simultaneously dependent of pressure and soluble solid concentration (Equation 3).

$$\Delta T_B = \alpha W^{\beta}\, exp\left(\gamma W\right) P^{\delta} \tag{3}$$

In Equation (3), $\Delta T_B = T_A - T_{A0}$ is the boiling point elevation (K) of the meat extract, W represents the mass concentration of soluble solids (ºBrix), P the absolute pressure (Pa) and α, β, γ and δ are the model parameters.

Specific heat

The specific heat (c_p, kJ/kg K) of the meat extract samples was measured in triplicate in the temperature range of 5 – 95 ºC by differential scanning calorimeter using a DSC 8000 apparatus (Perkin Elmer, Shelton, USA). Calibration of the DSC apparatus was made previously with indium (m.p. 156.6 °C, ΔH_f = 28.45 kJ/kg) at heating rate of 10 ºC/min. The purge gas was nitrogen (99.5% purity) flowing at ~20 mL/min. Aluminum pans of 24.01 ± 0.04 mg (ref. 0219-0062, Perkin Elmer, USA) were used for determining the baseline and also as holder for the reference material, the sapphire standard disk of 3-mm diameter [16] (ref. 0219-1268, Perkin Elmer, USA), and the meat extract samples. Samples were sealed and weighed before and after experimental procedures. Empty pans, reference material, and samples were subjected to the following thermal programs: isothermal at 0 ºC for 4 min, heating rate at 10 ºC/min up to 95 ºC, and isothermal at 95 ºC for 4 min, according to the procedures of the American Society for Testing and Materials ASTM-E1269 method [17]. The software PYRIS 11.0 (Perkin Elmer, Shelton, USA) was used to analyze and plot the thermal data. The specific heat was calculated using Equation (4):

$$c_p = c_{p_{ST}} \frac{D_S W_{ST}}{D_{ST} W_S} \tag{4}$$

where D_S is the vertical displacement between the thermal curves of the sample and the reference material at a given temperature (mW), D_{ST} is the vertical displacement between the thermal curves of the sapphire standard disks at a given temperature (mW), W_S is the sample mass (mg), W_{ST} is the sapphire standard disk mass (mg) and $c_{p_{ST}}$ is the specific heat of sapphire standard disk at a given temperature available in Archer [16] with accuracy of 0.0001 $J \cdot g^{-1} \cdot K^{-1}$. Mathematical modeling of specific heat data was carried out using empirical models depending on the soluble solid mass concentration and temperature given by:

$$c_p = \alpha_1 + \alpha_2 W + \alpha_3 W^2 + \alpha_4 T \tag{5}$$

$$c_p = \alpha_1 + \alpha_2 W + \alpha_4 T \tag{6}$$

$$c_p = \alpha_1 + \alpha_2 W \quad (7)$$

$$c_p = \alpha_1 + \alpha_4 T \quad (8)$$

In Equations (5) – (8), α_1, α_2, α_3, α_4, are the empirical model parameters, W is the soluble solid concentration (°Brix) and T is the temperature (K).

Statistical analysis

Regression analysis of boiling point elevation and specific heat data were carried out using non-linear regressions tool of the software OriginPro 8.0 (OriginLab Corporation, Northampton, USA). The coefficient of determination (R^2) and the mean relative error (MRE) were used to evaluate the quality of fitting and accuracy of the estimation, respectively. An F test was applied to verify the significant differences among the predicting models for specific heat. The simpler model with good representativeness was chosen to express specific heat as a function of the significant studied parameters.

RESULTS AND DISCUSSION

Boiling point elevation

Experimental values for boiling point temperature of meat extract (T_A) as a function of pressure and soluble solid concentration are presented in Figure 3A. In the pressure range of 3695.4 to 98173.9 Pa and meat extract concentrations from 1 to 60 °Brix, the experimental values of T_A varied from 27.9 to 106 ºC. In addition, the boiling point temperature of pure water (T_{A0}) was calculated in the same pressure range (3695.4 – 98173.9 Pa), resulting in values between 27.72 and 99.12 ºC.

As it was expected, the boiling point of meat extract increased with increasing pressure and soluble solid concentration. Similar behavior was observed for T_{A0} values as a function of pressure. The higher values of T_A when compared with T_{A0} at each level of pressure can be attributed to the mixture meat extract + water that present a little higher specific heat capacity than pure water. According to Darros-Barbosa et al. [18], foodstuffs in aqueous solution have a stronger deviation from pure water boiling point temperature at higher concentrations, due to a relative increase of the specific heat capacity. This is probably related to the difference in the equilibrium isomeric composition of aqueous solutions of hydrated solutes; less water-compatible solutes would lead to more disturbed hydration layer, and consequently to T_A higher than ideality. Similar behavior was reported for products as D-glucose and D-fructose solutions [19], blackberry juice [11] and aqueous solutions of mate [20].

To examine the relationship between T_A and T_{A0} values, the Dühring's rule (Equation 1) was applied. The corresponding results for the model fitting and statistical analysis are presented in Table 1. There was a good agreement between the proposed model and the experimental data, as evidenced by the high values of the coefficient of determination, $R^2 > 0.999$, and low mean relative error, $MRE < 0.041\%$, obtained for all levels of meat extract concentration. The good accuracy of the linear model to predicting T_A data from the theoretical data of T_{A0} at all concentration levels (Figure 3B) indicates a strong reliability of the methodology used to measure this thermodynamic property. Furthermore, values of the parameter m_0 showed a tendency to decrease as the meat extract concentration increases, whereas, values of m_1 increased as the meat extract concentration increases, in a similar trend to that reported by Gabas et al. [11].

An alternative way of correlating the dependence of boiling point on pressure is based on extending the use of expressions suitable for describing the temperature dependence of pure water vapor pressure, as in the case of the Antoine equation (Equation 2). The results of this model adjustment to the experimental data obtained for meat extract, at each soluble solid concentration studied, are also presented in Table 1. The statistical analysis indicated that this model can also be used to describe the experimental data, since R^2 values were higher than 0.999 and *MRE* (%) was lower than 0.108. The parameters A and C decreased when concentration of meat extract increased, whereas parameter B increased with increasing concentration. This finding is in close agreement with analogous results reported in literature for similar products, such as coffee extract [10] and solutions of mate [20]. The goodness of the agreement between experimental and theoretical values of $\ln(P)$ as a function of T_A and concentration can be observed in Figure 3C, establishing an explicit dependence of the model constants as a function of soluble solids content of meat extract [12].

A third correlation is presented in terms of the rise in boiling point (ΔT_B, K) according to Equation (3). Table 2 shows a very good agreement of the model with the experimental data, revealed by a high determination coefficient (R^2 = 0.991) as well as a low mean relative error (*MRE* = 14.19%). The accuracy of Equation (3) for predicting the elevation of boiling point of meat extract can also be seen by the fitted surface shown in Figure 3D. Values of parameters α, β, γ, and δ shown in Table 2 are in accordance to those published for other food products, such as coffee extract [10], apple juice and sugar solutions [15], and blackberry juice [11].

In general, the three examined correlation, the Dühring's rule, Antoine equation and Crapiste and Lozano equation, could be successfully used for describing the thermodynamic property T_A as a function of pressure (P), meat extract concentration (W) and boiling point temperature of pure water (T_{A0}). These correlations have great importance in designing and simulation of evaporation systems.

Specific heat

The experimental values of c_p varied from 2.214 to 4.140 kJ/ kg K in the temperature range of 5 to 95 °C and meat extract concentration between 1.5 and 60 °Brix. These values are similar to those reported for apple [21], reconstituted milk [22], and acerola and blueberry pulps [23]. When comparing the experimental values of c_p for meat extract to those estimated by the classical method of Choi and Okos [24] using the compositional data presented in item 2.1, a mean relative error of 6.57% was observed. So, linear and quadratic models were proposed to correlate the specific heat as a function of meat extract concentration (W) and temperature (T). Comparing the four models (Equations 5 to 8), the model that included the quadratic dependence on soluble solid concentration and linear dependence on temperature (Equation 5) resulted in the best fitting with values of $R^2 = 0.997$ and $MRE = 0.657\%$ (Table 3) and significant difference at 95% when analyzing variances among each model according to the F test, where calculated F were much higher than tabulated F for all comparisons.

Figure 3E shows the experimental of specific heat using the selected fitting model (Equation 5), in which it is expressed the linear and quadratic dependence of c_P on the meat extract concentration, and the linear behavior in relation to temperature. In addition, it is possible to state that the concentration effect is more prominent than the influence of temperature.

CONCLUSION

Boiling point elevation and specific heat capacity for meat extract were determined experimentally at different conditions of concentration and temperature encountered in the processing plants. For the boiling temperature, a group of three correlations (Dühring's rule, Antoine equation and Crapiste and Lozano equation) were evaluated and all of them gave excellent adjustment results, although the Crapiste and Lozano model is recommended for practical purposes, since it includes the simultaneous dependence on pressure and soluble solid concentration. Four empirical equations were tested to fit the specific heat data as a function of temperature and meat extract concentration, and the model including quadratic dependence on soluble solid concentration and linear dependence on temperature presented the best statistical parameters, supporting the fitting procedure and being able to describe the heat specific variations in a convenient form. The utility of the reported data is recommended in order to optimize the evaporation system design and performance, avoiding the underestimation of heat transfer areas and the overestimation of steam consumption. This aim can also be reached by the correct determination of global heat-transfer coefficients through the use of reported data along with the thermal conductivity and rheological properties of meat extract as function of temperature and solid concentration.

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Nomenclature

ΔT_B	Boiling point elevation (K)
$\Delta \mathrm{H_f}$	Fusion enthalpy (kJ/kg)
P	Pressure (mmHg; Pa)
c_p	Specific heat of the sample (kJ/kg K)

$c_{p_{ST}}$	Specific heat of the sapphire disk (kJ/kg K)
D_S	Vertical displacement between the thermal curves of the sample and the reference material at a given temperature (mW)
D_{ST}	Vertical displacement between the thermal curves of the sapphire standard disk and the reference material at a given temperature (mW)
W_S	Sample mass used in the DSC calculation (mg)
W_{ST}	Sapphire disk mass used in the DSC calculation (mg)
W	Solids concentration (ºBrix)
T	Temperature (K)
T_{A0}	Pure water boiling point at a given pressure (K)
T_A	Boiling point of meat extract at a given pressure (K)
A, B, C	Parameters of the Antoine equation
MRE	Mean relative error (%)
R^2	Coefficient of determination (dimensionless)
m_0, m_1	Parameters in Dühring’s rule (K; dimensionless)
Greek symbols	
$\alpha, \beta, \gamma, \delta$	Parameters in Crapiste and Lozano’s model
$\alpha_1, \alpha_2, \alpha_3, \alpha_4$	Parameters used in specific heat modeling

Table 1. Fitted parameters for Dühring’s rule (Eq. 1) and Antonie Equation (Eq. 2) of meat extract at different soluble solid concentrations.

W (°Brix)	Dühring's rule				Antoine Equation			
	Parameter	Value	R^2	*MRE* (%)	Parameter	Value	R^2	*MRE* (%)
1	m_0	-1.025	0.999	0.017	*A*	18.603	0.999	0.050
					B	4019.1		
	m_1	1.004			*C*	-37.922		
5	m_0	-1.235	0.999	0.017	*A*	18.600	0.999	0.047
					B	4019.6		
	m_1	1.005			*C*	-37.919		
10	m_0	-1.280	0.999	0.018	*A*	18.604	0.999	0.058
					B	4020.6		
	m_1	1.005			*C*	-38.004		
20	m_0	-1.202	0.999	0.013	*A*	18.587	0.999	0.035
					B	4022.7		
	m_1	1.007			*C*	-38.196		
30	m_0	-1.996	0.999	0.019	*A*	18.564	0.999	0.052
					B	4026.6		
	m_1	1.012			*C*	-38.163		
35	m_0	-2.568	0.999	0.015	*A*	18.553	0.999	0.044
					B	4027.7		
	m_1	1.014			*C*	-38.057		
40	m_0	-3.373	0.999	0.019	*A*	18.529	0.999	0.053
					B	4032.3		
	m_1	1.019			*C*	-38.086		
45	m_0	-3.856	0.999	0.041	*A*	17.661	0.999	0.108
					B	4034.8		
	m_1	1.022			*C*	-37.99		
50	m_0	-4.138	0.999	0.036	*A*	18.503	0.999	0.102
					B	4037.1		
	m_1	1.024			*C*	-38.08		
55	m_0	-4.994	0.999	0.025	*A*	18.482	0.999	0.067
					B	4039.8		
	m_1	1.029			*C*	-38.109		
60	m_0	-6.176	0.999	0.029	*A*	18.446	0.999	0.081
	m	1.035			*B*	4044.6		

C	-37.936

Table 2. Fitting parameters for the model correlating the boiling point elevation (ΔT_B) as a function of pressure and soluble solid concentration (Equation 3).

Parameter	Value	R^2	*MRE* (%)
α	0.052	0.991	14.19
β	0.466		
γ	0.024		
δ	0.135		

Table 3. Fitting parameters for the proposed models correlating the specific heat (c_p) as a function of temperature and soluble solid concentration.

Model	Parameter	Value	R^2	*MRE* (%)
Eq. (5)	α_1	3.072	0.997	0.657
	α_2	-0.026		
	α_3	-3.284×10^{-5}		
	α_4	3.074×10^{-3}		
Eq. (6)	α_1	3.091	0.997	0.700
	α_2	-2.859×10^{-2}		
	α_4	3.074×10^{-3}		
Eq. (7)	α_1	4.084	0.970	2.475
	α_2	-2.859×10^{-2}		
Eq. (8)	α_1	2.230	0.027	14.996
	α_4	3.074×10^{-3}		

Figure 1. Schematically representation of the meat broth concentration process: **(a)** sterilization step; **(b)** three-effect evaporation system.

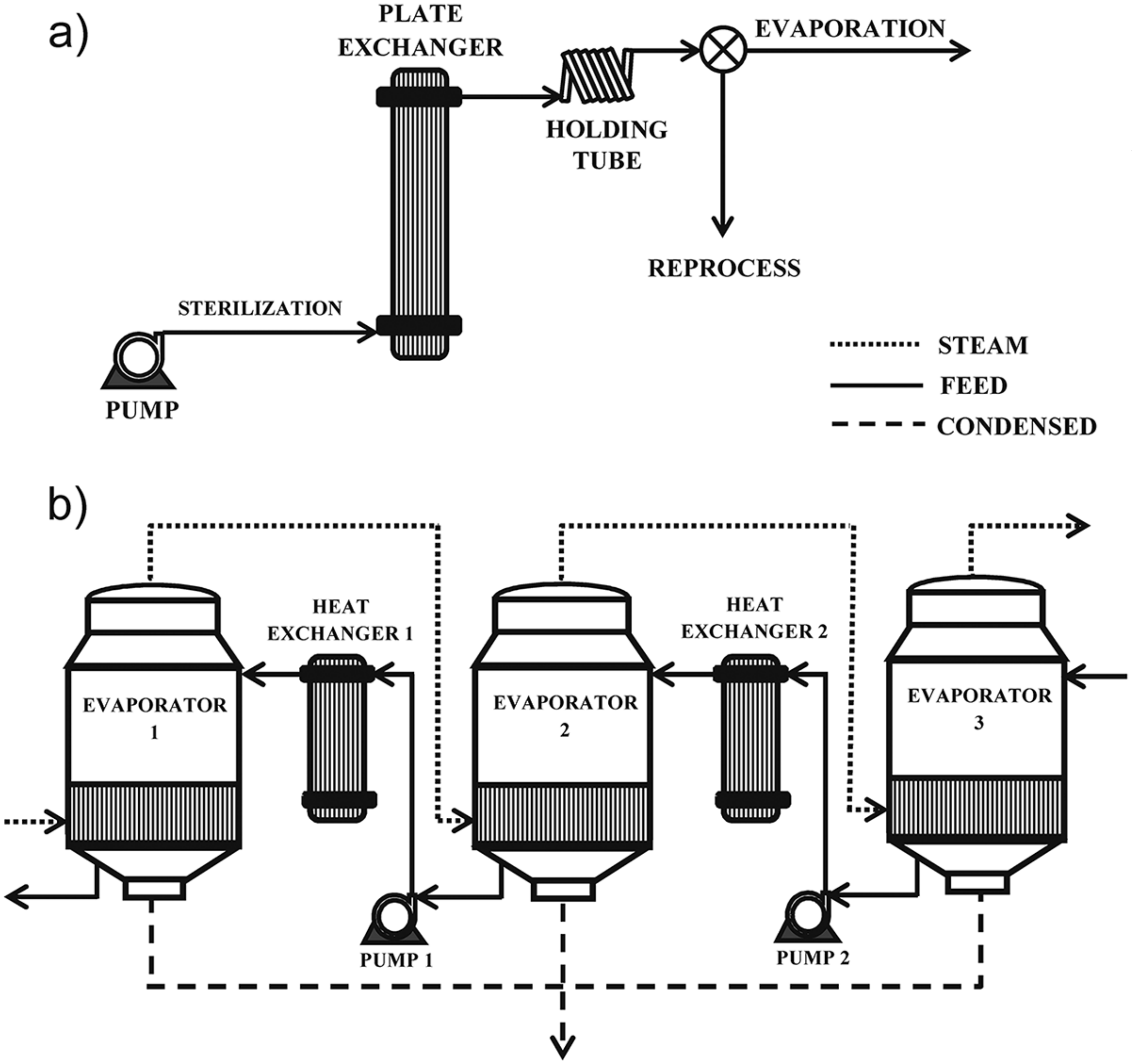

Figure 2. Apparatus used for experimental measurement of boiling point temperature.

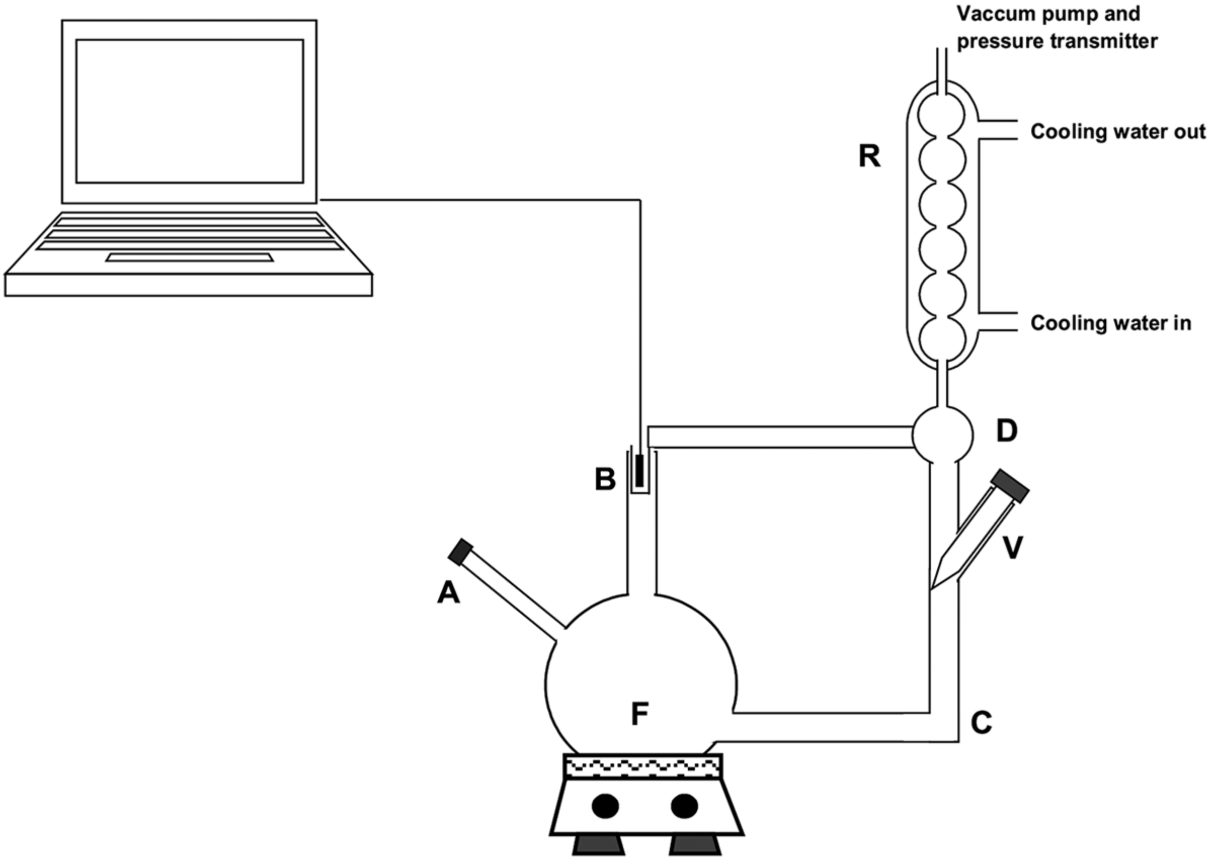

Figure 3. A: Experimental values for boiling point temperature of meat extract (T_A) as a function of pressure (P) and soluble solids concentration (W); **B:** Dependence of T_A on the boiling point of pure water at the same pressure (T_{A0}) and W; **C:** Dependence of meat extract vapor pressure ($ln\ P$) on T_A and on W using Equation (2); **D:** Dependence of the boiling point elevation (ΔT_B) of meat extract P and on W using Equation (3); **E:** Dependence of the specific heat (c_P) of meat extract on temperature (T) and on W using the best model fitted (Equation 5).