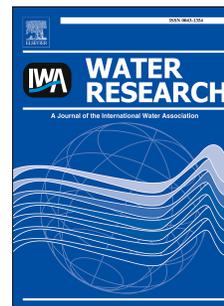


# Accepted Manuscript

New systematic methodology for incorporating dynamic heat transfer modelling in multi-phase biochemical reactors

T. Fernández-Arévalo, I. Lizarralde, P. Grau, E. Ayesa



PII: S0043-1354(14)00319-4

DOI: [10.1016/j.watres.2014.04.034](https://doi.org/10.1016/j.watres.2014.04.034)

Reference: WR 10636

To appear in: *Water Research*

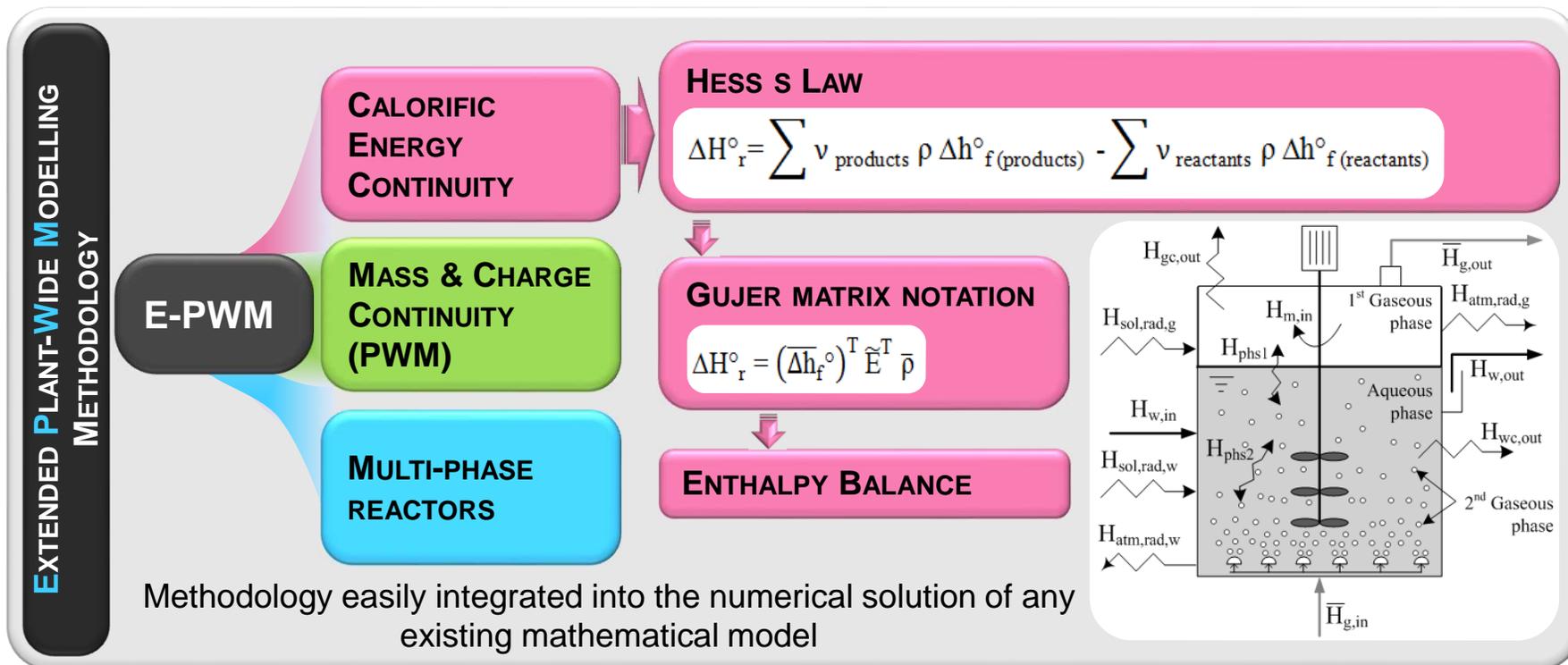
Received Date: 17 September 2013

Revised Date: 17 January 2014

Accepted Date: 18 April 2014

Please cite this article as: Fernández-Arévalo, T., Lizarralde, I., Grau, P., Ayesa, E., New systematic methodology for incorporating dynamic heat transfer modelling in multi-phase biochemical reactors, *Water Research* (2014), doi: 10.1016/j.watres.2014.04.034.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



1 **New systematic methodology for incorporating dynamic heat transfer modelling**  
2 **in multi-phase biochemical reactors**

3  
4 T. Fernández-Arévalo, I. Lizarralde, P. Grau and E. Ayesa

5  
6 CEIT and Tecnun (University of Navarra), 15 Paseo Manuel de Lardizabal, San Sebastián 20018,

7 Spain

8 (E-mail: [tfernandez@ceit.es](mailto:tfernandez@ceit.es); [ilizarralde@ceit.es](mailto:ilizarralde@ceit.es); [pgrau@ceit.es](mailto:pgrau@ceit.es); [eayesa@ceit.es](mailto:eayesa@ceit.es))

9  
10 **Abstract**

11 This paper presents a new modelling methodology for dynamically predicting the heat  
12 produced or consumed in the transformations of any biological reactor using Hess's law.  
13 Starting from a complete description of model components stoichiometry and formation  
14 enthalpies, the proposed modelling methodology has integrated successfully the  
15 simultaneous calculation of both the conventional mass balances and the enthalpy change  
16 of reaction in an expandable multi-phase matrix structure, which facilitates a detailed  
17 prediction of the main heat fluxes in the biochemical reactors. The methodology has been  
18 implemented in a plant-wide modelling methodology in order to facilitate the dynamic  
19 description of mass and heat throughout the plant. After validation with literature data, as  
20 illustrative examples of the capability of the methodology, two case studies have been  
21 described. In the first one, a predenitrification-nitrification dynamic process has been  
22 analysed, with the aim of demonstrating the easy integration of the methodology in any  
23 system. In the second case study, the simulation of a thermal model for an ATAD has  
24 shown the potential of the proposed methodology for analysing the effect of ventilation and  
25 influent characterization.

27 **Keywords**

28 Heat balance; Hess's law; Mathematical modelling; Multi-phase models; Plant-Wide Modelling

29 methodology

30

31 **NOMENCLATURE**

$A_{\text{bubbles}}$	Contact area between aqueous phase and 2 <sup>nd</sup> gas phase (m <sup>2</sup> )
$A_{\text{g}}$	1 <sup>st</sup> gas phase surrounding area (m <sup>2</sup> )
$A_{\text{tank}}$	Contact area between aqueous phase and 1 <sup>st</sup> gas phase (m <sup>2</sup> )
$A_{\text{w}}$	Aqueous phase surrounding area (m <sup>2</sup> )
$\overline{Cp}_i$	Specific heat capacity of i gaseous phase components at constant pressure (kJ gE <sup>-1</sup> K <sup>-1</sup> )
$Cp_{\text{w,H}_2\text{O}}$	Specific heat capacity of water at constant pressure (kJ gH <sub>2</sub> O <sup>-1</sup> K <sup>-1</sup> )
$\tilde{E}_{ij}$	i phase stoichiometric matrix for the transformations between i and j phase
$g$	Gravitational acceleration (m s <sup>-2</sup> )
$Gr$	Grashof number
$\bar{h}_{i,\text{ref}}$	Reference enthalpy of the i gaseous phase components (kJ gE <sup>-1</sup> )
$h_{\text{w,ref,H}_2\text{O}}$	Reference enthalpy of water (kJ gH <sub>2</sub> O <sup>-1</sup> )
$H_{\text{Act}}$	Enthalpy transmitted from the actuators (kJ d <sup>-1</sup> )
$H_{\text{atm\_rad}}$	Longwave atmospheric radiation flux (kJ d <sup>-1</sup> )
$H_{\text{Cond/Conv}}$	Surface conduction and convection enthalpy flux (kJ d <sup>-1</sup> )
$\bar{H}_{\text{in}}$	Input enthalpy (kJ d <sup>-1</sup> )
$\bar{H}_{\text{out}}$	Output enthalpy (kJ d <sup>-1</sup> )
$H_{\text{sol\_rad}}$	Shortwave solar radiation flux (kJ d <sup>-1</sup> )
$H_{\text{T}}$	Net heat exchange of the analysed phase (kJ d <sup>-1</sup> )
$H_{\text{trans}}$	Heat released or absorbed by the transformations in the analysed phase (kJ d <sup>-1</sup> )
$k_{\text{sol,rad}}$	Total energy incident on the surface (kJ d <sup>-1</sup> m <sup>-2</sup> )
$k_{\text{wls}}$	Heat conduction through walls and pipes coefficient (kJ d <sup>-1</sup> K <sup>-1</sup> m <sup>-2</sup> )
$\bar{m}_{i,\text{in}}$	Inlet i phase mass flux (gE d <sup>-1</sup> )
$\bar{m}_{i,j}$	Mass flux transport between i and j phases (gE d <sup>-1</sup> )
$\bar{m}_{i,\text{out}}$	Outlet i phase mass flux (gE d <sup>-1</sup> )
$\bar{M}_i$	Mass vector for the components present in the i phase (gE)

$n_{\text{phs},i}$	Constant exponent of the Pr and Gr numbers (aqueous and i gaseous phases conduction/convection)
NC	No. of components in the i phase
NT	No. of transformations in the i phase
$P_m$	Power supplied by the engines and aeration systems ( $\text{kJ d}^{-1}$ )
Pr	Prandtl number
$T_{\text{atm}}$	Atmospheric temperature (K)
$T_i$	i phase temperature (K)
$T_{i,\text{in}}$	i phase inflow temperature (K)
$\bar{T}_{i,\text{ref}}$	Temperature corresponding to the reference enthalpy of the i gaseous phase components (K)
$T_{\text{w,ref,H2O}}$	Temperature corresponding to the reference enthalpy of water (K)
$\bar{X}_i$	Mass fraction of the gaseous phase components ( $\text{gE}_i \text{gE}_{\text{phase}}^{-1}$ )

### Greek Symbols

$\alpha_{\text{phs},i}$	Correction factor for surfaces facing up (aqueous and i gaseous phases conduction/convection)
$\alpha_{\text{rad}}$	Solar absorptivity
$\beta_{\text{air}}$	Atmospheric radiation factor
$\beta_{\text{phs}}$	Coefficient of volume expansion ( $\text{K}^{-1}$ )
$\delta$	Characteristic length (m)
$\Delta h_f$	Specific formation enthalpy ( $\text{kJ gE}^{-1}$ )
$\Delta h_r$	Specific reaction enthalpy ( $\text{kJ gE}^{-1}$ )
$\Delta H_r$	Net reaction enthalpy ( $\text{kJ d}^{-1}$ )
$\varepsilon_{\text{atm}}$	Surface emissivity
$\eta_m$	Efficiency of engines/aeration systems
$\bar{\lambda}_i$	Thermal conductivity of the i gaseous phase components ( $\text{kJ d}^{-1} \text{K}^{-1} \text{m}^{-1}$ )
$\lambda_{\text{atm}}$	Surface reflectivity
$\mu_{\text{gl}}$	Dynamic viscosity of the gaseous phase components ( $\text{kgE m}^{-1} \text{s}^{-1}$ )
$v_{i,j}$	Rate coefficient for component i on process j ( $\text{gE}_i \text{gE}_{\text{reference component}}^{-1}$ )
$\bar{p}_{i,j}$	Kinetic rate for the transformations between i and j phases ( $\text{gE}_{\text{removed component}} \text{d}^{-1}$ )
$\sigma$	Stefan Boltzman constant ( $\text{kJ d}^{-1} \text{m}^{-2} \text{K}^{-4}$ )
$\nu_{\text{gl}}$	Kinematic viscosity of the gaseous phase components ( $\text{m}^2 \text{s}^{-1}$ )

### Superscripts

*	Absolute temperature (°C)
°	Standard state values (25°C)

**Subscripts**

g	gaseous phase
g <sub>1</sub>	1 <sup>st</sup> gaseous phase
g <sub>2</sub>	2 <sup>nd</sup> gaseous phase
in	Input
k	No. of state variables in the water phase
m	No. of state variables in the 1 <sup>st</sup> gaseous phase
n	No. of transformations in the water phase
out	Output
s	solid phase
z	No. of state variables in the 2 <sup>nd</sup> gaseous phase
w	Aqueous phase

32

33 **1. INTRODUCTION**

34 Operating temperature plays an important role in wastewater treatment efficiency (Metcalf and  
35 Eddy, 2004). Temperature dynamics affect microbial activity as well as physicochemical properties,  
36 such as dissolved oxygen saturation concentration, diffusivity, viscosity, density and the settling  
37 velocity (Sedory and Stenstrom 1995). An increased temperature of a few degrees might stimulate  
38 the metabolic activity of the bacteria, while a substantial reduction of several degrees would result  
39 in reduced process stability, albeit temporarily, and a possible shift in the population of the reactor  
40 (Gallert and Winter, 2005). The causes of these temperature variations are often due to a  
41 combination of different factors. The most representative are conduction/convection phenomena,  
42 short-wave and long-wave radiations, the heat transmitted by the actuators and, to a greater or lesser  
43 degree, the heat produced or consumed by biochemical, chemical or physico-chemical  
44 transformations. The influence of each term in the system is varied and depends largely on the  
45 analysed process and climate of the place. In the activated sludge units, a typical diurnal

46 temperature difference between water inlet and outlet fluxes only varies between 0.5 and 1 degree  
47 (Makinia *et al.*, 2005). However, in some parts of the world, treatment systems are subjected to  
48 significant winter cooling and summer heating. In some nontemperate zones for instance, the  
49 atmospheric diurnal air temperature variation can be considerable, ranging from 2 degrees during  
50 the early morning to over 25 degrees during mid-afternoon (Paul, 2013), affecting considerably to  
51 the water temperature. In membrane bioreactors, the temperature rise in the tank may be quite  
52 significant comparing with the activated sludge reactors because of the higher biological heat  
53 production. These reactors have a higher biomass concentration and bacterial activity, which  
54 implies a higher biological heat production due to the exothermicity of the oxidation, nitrification  
55 and denitrification reactions (Sethi *et al.*, 2011). In sludge line processes, the effect of temperature  
56 has greater importance and practically all units work above atmospheric temperature. The anaerobic  
57 digestion for example, is often an endothermic process which operates around 35 or 55 degrees,  
58 thus requiring a heat supply to maintain the digester temperature and support the microbial activity  
59 (Inoije *et al.*, 1996), and in the Autothermal Thermophilic Aerobic Digestion (ATAD) the organic  
60 matter is oxidized under aerobic conditions with a concomitant biological heat release that is able to  
61 maintain thermophilic temperatures. Despite the clear knowledge that exists to date on the  
62 phenomena involved in the transfer of heat, the exact influence of temperature is difficult to  
63 determine because of its interaction with mass transfer, chemical equilibrium and growth rate (Van  
64 Hulle *et al.*, 2010). It is for this reason that the joint modelling of biological transformations and  
65 accurate heat transfer models are becoming increasingly practical and necessary, not only to predict  
66 the temperature of the system, but also to identify the diverse heat flows, to analyse the contribution  
67 of these in the heat transfers, to relate the temperature variations with the chemical, biochemical and  
68 physico-chemical transformations and, ultimately, to understand the process better. An accurate  
69 temperature model allows determining a precise microbial activity, which is extremely important  
70 aspect in the analysis of new operational strategies as well as new configurations

71 (www.novedar.com). Nowadays, thermal processes are increasingly being incorporated into  
72 treatment plants (Daigger, 2011), making temperature prediction models essential for a proper use  
73 and recovery of the heat.

74

75 Nonetheless, most of the existing mathematical models of activated sludge units and anaerobic  
76 digestion models focus mainly on microbiology and often assume constant temperature (Makinia *et*  
77 *al.*, 2005). There are several papers which have included temperature prediction in the general  
78 model, the studies carried out by Novotny and Krenkel (1973), Argaman and Adams (1977),  
79 Sedony and Stenstrom (1995), la Cour Jansen *et al.* (1992), Gillot and Vanrolleghem (2003),  
80 Makinia *et al.* (2005) and Lippi *et al.* (2009) being some of the most representative works in water  
81 line modelling. In the field of municipal sludge digestion, almost all heat transfer models published  
82 in literature focus on the representation of the ATAD (Vismara, 1985; Messenger *et al.*, 1992 &  
83 1993; Pitt *et al.*, 1994; Lapara *et al.*, 1999; Gómez *et al.*, 2007; and de Gracia *et al.*, 2009), focusing  
84 less on anaerobic digestion. All these publications propose a detailed and accurate heat transfer  
85 model for a precise prediction of the temperature. However, most of them are very specific for the  
86 system under study, with a limited capacity for being expanded or adapted to include additional  
87 transformations in water or gas phases. Moreover, the description of heat generated or consumed in  
88 biochemical transformations are normally only based on COD removal. Therefore, a rigorous and  
89 systematic methodology for constructing more detailed and flexible heat transfer models in  
90 biochemical reactors is demanded.

91 Observing the low-detail used in the definition of the reaction heat, the first goal of this work has  
92 been the development of a systematic, generic and rigorous methodology for the dynamic prediction  
93 of the heat produced and consumed in all transformations of any biological reactor. And, the second  
94 goal has been the restructuration of the mass and heat balances to allow the modeller to construct  
95 mathematical models as complex as required in a systematic and modular way.

96

97 The complexity of today configurations and processes with recirculations and interrelations among  
98 the different units makes it necessary to consider a plant-wide perspective in order to establish an  
99 optimum solution for the design or operation of entire plants (Copp *et al.*, 2003; Grau *et al.* 2007;  
100 Jeppsson *et al.*, 2007). The PWM methodology (Grau *et al.*, 2007) was proposed by the CEIT as a  
101 systematic methodology for constructing mathematical models able to describe the whole plant as  
102 complex as required in each case study. Along these years, the premises in which this methodology  
103 was based (elemental mass characterisation) have been demonstrated as the most suitable  
104 framework for developing mathematical models able to face with current needs, such as the  
105 technologies where liquid, gaseous and solids phases coexist with energetic aspects. With this  
106 frame, an update of the Plant-Wide Modelling (PWM; Grau *et al.*, 2007) methodology has been  
107 carried out in order to describe technologies in which not only the water phase is considered but  
108 also the gas phase in contact with it and the transfers among them and to incorporate heat balances  
109 that allow a better estimation of process temperature and a proper use and recovery of the heat.

110

## 111 **2. EXTENDED PLANT-WIDE MODELLING METHODOLOGY (E-PWM)**

112 Plant-Wide Modelling (PWM) methodology (Grau *et al.*, 2007) was proposed for the systematic  
113 construction of compatible unit-process models for describing the dynamic behaviour of the water  
114 and sludge lines in an integrated way. This methodology is based on selecting the set of process  
115 transformations required to model all unit-process elements incorporated into each specific WWTP.  
116 For the unification and standardisation of this set of biochemical, chemical and physico-chemical  
117 transformations, the incorporation of activation/inhibition terms in the kinetics must be accurate, in  
118 order to reproduce the appropriate bacterial activity under aerobic, anoxic and anaerobic conditions.  
119 Additionally, this unification permits the definition of a unique component vector for the whole  
120 plant, without the need to develop specific transformers to interface the unit-process models,

121 making it a flexible methodology for both the definition of new reactions or processes and defining  
122 new units. The accurate definition of the stoichiometry ensures the elemental mass (in terms of C,  
123 N, O, H, P or other additional elements) and charge continuity in all the transformations. In order to  
124 achieve this, some components must act as source-sink terms (or mass “compensation terms”) for  
125 the correct adjustment of the C, N, O, H, P and charge balances (Reichert *et al.*, 2001; de Gracia *et*  
126 *al.*, 2006). More details of this methodology can be found in Grau *et al.* (2007).

127

128 In this paper an update of PWM called Extended Plant-Wide Modelling methodology (E-PWM) is  
129 proposed. This update is focused on facilitating the modelling of heat transfer phenomena in multi-  
130 phase biochemical reactors. For this purpose, the methodology has been based mainly on two  
131 aspects: (1) the multi-phase structure of the mathematical model and (2) the incorporation of  
132 generic heat transfer models based on the automatic calculation of the enthalpy change of reaction  
133 associated with all transformations of the system.

134

### 135 **2.1. Multi-phase model construction in the Extended Plant-Wide Modelling methodology**

136 The description of ASM models (Henze *et al.*, 2000) is based on the Gujer matrix notation that  
137 presents the process kinetics and stoichiometry in a single product of matrices ( $\tilde{E} \cdot \bar{p}$ ). These models  
138 only considered the water phase reactions, but in current technologies different aqueous, gaseous or  
139 solid phases can be considered in a single unit-process multiplying the equations required to models  
140 definition. With the purpose to develop flexible and easily understood models, the E-PWM  
141 methodology proposes a general procedure for multi-phase model construction in which mass  
142 balances are constructed systematically considering as many type of phases (gas, liquid, solid) and  
143 number (1 liquid + 1 gas, 1 liquid + 2 gas phases, etc.) as required in each case study. The first step  
144 of the procedure consists on the selection of the phases and transformations to model the WWTP  
145 under study. Each phase (aqueous, gaseous or solid) as an independent system with its

146 corresponding mass vector ( $\bar{M}$ ) will be considered. Accordingly, each phase will have an  
 147 independent matrix ( $\tilde{E} \cdot \bar{\rho}$ ) to define the transformations that take place in the phase (such as, for  
 148 example, bacterial growth, or chemical equilibria reactions in the aqueous phase) and another set of  
 149 matrices ( $\tilde{E} \cdot \bar{\rho}$ ) to define the transformations between different phases (such as  
 150 evaporation/condensation, stripping/absorption, precipitation/dissolution or deposition/sublimation).  
 151 Thus, the model will be constructed using as many matrices as phases and interactions between  
 152 phases. This modular construction can be visualized by means of the generic example depicted in  
 153 Figure 1. And the second step consists on the definition of the mass balances of the unit processes.  
 154 The definition of the set of matrices allows a systematic mass balance description based on the  
 155 structure shown in equation 1.

$$\left(\frac{d\bar{M}}{dt}\right)_i = \tilde{E}_{i,i}^T \bar{\rho}_{i,i} + \sum_{j=1}^{\text{No. adj. phase}} \tilde{E}_{i,j}^T \bar{\rho}_{i,j} + \sum_{\text{in}} \bar{m}_{\text{phase}} - \sum_{\text{out}} \bar{m}_{\text{phase}} \quad (1)$$

156  $i = 1, 2 \dots \text{No. phases (number of phases)}$   
 157  $j = 1, 2 \dots \text{No. adj. phase (number of adjacent phases to phase } i)$

158 Thus, the mass balance in each phase will be constructed as follows: the matrix ( $\tilde{E}_{i,i} \cdot \bar{\rho}_{i,i}$ ) with the  
 159 transformations that take place in the phase, plus the matrix with the transformations between  
 160 different phases ( $\tilde{E}_{i,j} \bar{\rho}_{i,j}$ ), plus the mass inputs and outputs of the system.

161  
 162 This way of distinguishing the different phases and applying mass balances in each one, enables the  
 163 modeller to construct systematically mathematical models as complex as required, considering  
 164 different aqueous, gaseous or solid phases in a single unit-process. For example, in the case of  
 165 layered models for settlers or biofilm systems in which biological reactions need to be included,  
 166 each layer is considered to be an aqueous phase and mass transfers among them due to diffusion,  
 167 convection or gravity effects are described by means of a stoichiometric matrix and kinetic vector.  
 168 To understand better this methodology, an example is shown in section 3.

169

170 **2.2. New methodology for temperature prediction based on formation enthalpies**

171 As previously mentioned, the PWM methodology is based on the components characterization in  
 172 their elemental mass and charge density. This quality is essential to avoid redundancies in  
 173 component definition and to guarantee elemental mass and charge continuity throughout the whole  
 174 plant. This detailed components characterization is also the one that enables the estimation of  
 175 formation enthalpies for each model component and makes possible a systematic calculation of the  
 176 heat released or absorbed by each transformation, guaranteeing heat energy continuity at any point  
 177 in the plant. Thus, the specific enthalpy change of reaction ( $\Delta h_r^\circ$  in  $\text{kJ g}_{\text{stoich. unit}}^{-1}$ ) due to  
 178 biochemical, physico-chemical or chemical transformations can be defined as the difference  
 179 between the enthalpy of formation of the products and the enthalpy of formation of the reactants  
 180 (applying Hess's law).

$$\Delta h_r^\circ = \sum v_{\text{products}} \Delta h_{\text{f(products)}}^\circ - \sum v_{\text{reactants}} \Delta h_{\text{f(reactants)}}^\circ \quad (2)$$

181 To calculate the net enthalpy change of reaction ( $\Delta H_r^\circ$  in  $\text{KJ d}^{-1}$ ) instead, multiplying this specific  
 182 enthalpy change of reaction by its corresponding kinetic and stoichiometry is sufficient:

$$\Delta H_r^\circ = \sum v_{\text{products}} \rho \Delta h_{\text{f(products)}}^\circ - \sum v_{\text{reactants}} \rho \Delta h_{\text{f(reactants)}}^\circ \quad (3)$$

183 Therefore, the net enthalpy change (see Equation 5) can be expressed as a function of the well-  
 184 known Gujer transformation matrices (Equation 4; Henze *et al*, 2000) and the enthalpy of formation  
 185 vector ( $\overline{\Delta h_f^\circ}$ ).

$$\dot{x} = \tilde{E}^T \bar{\rho} \quad (4)$$

$$\Delta H_r^\circ = (\overline{\Delta h_f^\circ})^T \dot{x} \quad (5)$$

186 where,

$$\overline{\Delta h_f^\circ} = \begin{pmatrix} \Delta h_{f1} \\ \Delta h_{f2} \\ \vdots \\ \Delta h_{fj} \\ \vdots \\ \Delta h_{fk} \end{pmatrix}; \quad \tilde{E} = \begin{pmatrix} v_{11} & v_{12} & \dots & v_{1j} & \dots & v_{1k} \\ v_{21} & v_{22} & \dots & v_{2j} & \dots & v_{2k} \\ \vdots & \vdots & & \vdots & & \vdots \\ v_{i1} & v_{i2} & \dots & v_{ij} & \dots & v_{ik} \\ \vdots & \vdots & & \vdots & & \vdots \\ v_{n1} & v_{n2} & \dots & v_{nj} & \dots & v_{nk} \end{pmatrix}; \quad \bar{\rho} = \begin{pmatrix} \rho_1 \\ \rho_2 \\ \vdots \\ \rho_i \\ \vdots \\ \rho_n \end{pmatrix};$$

187 This close relationship maintaining mass and heat balances makes it a systematic methodology that  
 188 can be easily integrated into the numerical solution of any existing mathematical model. The only  
 189 requisite is the definition of the enthalpies of formation of the compounds present in these  
 190 transformations. For this paper a set of transformations have been selected from the E-PWM library  
 191 which gather all the components and transformations able to describe aerobic, anoxic and anaerobic  
 192 COD biodegradation; nitrogen removal in two steps ( $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2$ ); anaerobic ammonia  
 193 oxidation (Anammox process); aerobic or anaerobic sludge digestion; as well as, sludge  
 194 pretreatments. Enthalpies of formation needed for the definition of these transformations are  
 195 summarized in Table 1 and Table 2.

196

197 Most of these enthalpies of formation of of inorganic compounds, gaseous components and some  
 198 organic compounds have been found in chemical handbooks and in specialized databases. To  
 199 estimate the rest of enthalpies of formation by contrast, different methods and approaches have been  
 200 used, such as the molecular group contribution approach (Constantinou and Gani, 1994; Hukkerikar  
 201 *et al.*, 2013) or the strengths of bonds approach (Nelson *et al.*, 2005).

202

### 203 3. IMPLEMENTATION OF THE E-PWM METHODOLOGY IN AN AERATED 204 COMPLETELY STIRRED CLOSED TANK REACTOR

205 One illustrative example of the usefulness of the presented E-PWM methodology can be shown in  
 206 aerated biological closed reactors. In these, an aqueous phase coexists with two gaseous phases; one  
 207 corresponds to the total volume occupied by the bubbles submerged in the mixed liquor (gas hold-  
 208 up) and the other one to the volume of the gas in contact with the free surface of the mixed liquor

209 (off-gas). The distinction of these volumes represents an interesting advantage over other simpler  
 210 models, both for the oxygen transfer estimation, as for the correct prediction of the temperature in  
 211 each phase.

212

### 213 3.1. Mass balance for an aerated biological closed reactor

214 For the analysis of three phases, three mass balances are necessary, as shown in equations 6, 7, and

215 8.

$$\left(\frac{d\bar{M}_w}{dt}\right) = \tilde{E}_{w,w}^T \bar{\rho}_{w,w} + \tilde{E}_{w,g1}^T \bar{\rho}_{w,g1} + \tilde{E}_{w,g2}^T \bar{\rho}_{w,g2} + \bar{m}_{w,in} - \bar{m}_{w,out} \quad (6)$$

$$\left(\frac{d\bar{M}_{g1}}{dt}\right) = \tilde{E}_{g1,w}^T \bar{\rho}_{g1,w} + \bar{m}_{g2,g1} - \bar{m}_{g,out} \quad (7)$$

$$\left(\frac{d\bar{M}_{g2}}{dt}\right) = \tilde{E}_{g2,w}^T \bar{\rho}_{g2,w} + \bar{m}_{g,in} - \bar{m}_{g2,g1} \quad (8)$$

216 For this specific case, the assumptions listed below have been made: (1) perfect and continuous  
 217 mixing is assumed; (2) reactions in the gaseous phases have not been considered, only the aqueous  
 218 phase reactions; (3) the transition from the first gaseous phase (gas hold-up) to the second gaseous  
 219 phase (off-gas) has been defined as a mass transfer, and not as reaction. Thus, the first term of the  
 220 aqueous mass balance ( $\tilde{E}_{w,w}^T \bar{\rho}_{w,w}$ ) gathers all transformations that can take place in this phase  
 221 (such as biochemical reactions or chemical equilibria among others) and the remaining  
 222 transformations correspond to liquid-gas transfers ( $\tilde{E}_{i,j}^T \bar{\rho}_{i,j}$ ) such as evaporation/condensation or  
 223 stripping/absorption reactions (see Figure 2).

224

### 225 3.2. Heat balance for an aerated biological closed reactor

226 The completely mixing assumption commonly used in wastewater treatment plant process  
 227 modelling, permits thermal uniformity in the reactor, avoiding temperature gradients. Thus, based  
 228 on the energy conservation principle, the general one-dimensional dynamic heat transfer model

229 includes biochemical, chemical or physico-chemical heat transfers ( $H_{\text{trans}}$ ), conduction and  
 230 convection fluxes ( $H_{\text{Cond/Conv}}$ ), heat energy fluxes transmitted by the actuators ( $H_{\text{Act}}$ ) and short-  
 231 wave (solar) and long-wave (atmospheric) radiations ( $H_{\text{sol\_rad}}$ ,  $H_{\text{atm\_rad}}$ ), as can be shown in  
 232 equation 9.

$$\left(\frac{dH_T}{dt}\right)_{\text{phase}} = \sum H_{\text{trans}} + \sum H_{\text{Cond/Conv}} + \sum H_{\text{Act}} + \sum H_{\text{sol\_rad}} + \sum H_{\text{atm\_rad}} + \sum \bar{H}_{\text{in}} + \sum \bar{H}_{\text{out}} \quad (9)$$

233 The formulation for the time-derivative of enthalpy-state-variables has also followed the multi-  
 234 phase principle proposed. Thus, equation 9 is transformed into the following equations:

$$\begin{aligned} \left(\frac{dH_w}{dt}\right) = & -(\overline{\Delta h_{fw}})^T \left(\tilde{E}_{w,w}^T \bar{p}_{w,w}\right) - (\overline{\Delta h_{fw}})^T \left(\tilde{E}_{w,g1}^T \bar{p}_{w,g1}\right) - (\overline{\Delta h_{fg1}})^T \left(\tilde{E}_{g1,w}^T \bar{p}_{g1,w}\right) \\ & - (\overline{\Delta h_{fw}})^T \left(\tilde{E}_{w,g2}^T \bar{p}_{w,g2}\right) - (\overline{\Delta h_{fg2}})^T \left(\tilde{E}_{g2,w}^T \bar{p}_{g2,w}\right) + H_{w,g1} + H_{w,g2} + H_{w,\text{in}} - H_{w,\text{out}} \\ & - H_{\text{phs1}} - H_{\text{phs2}} - H_{\text{wc,out}} + H_{\text{m,in}} - H_{\text{atm,rad,w}} + H_{\text{sol,rad,w}} \end{aligned} \quad (10)$$

$$\left(\frac{dH_{g1}}{dt}\right) = \sum_{i=1}^m (\bar{H}_{g1,g2}) + \sum_{i=1}^m (\bar{H}_{g1,w}) - \sum_{i=1}^m (\bar{H}_{g,\text{out}}) + H_{\text{phs1}} - H_{\text{gc,out}} - H_{\text{atm,rad,g}} + H_{\text{sol,rad,g}} \quad (11)$$

$$\left(\frac{dH_{g2}}{dt}\right) = \sum_{i=1}^z (\bar{H}_{g,\text{in}}) + \sum_{i=1}^z (\bar{H}_{g2,w}) + \sum_{i=1}^z (\bar{H}_{g2,g1}) + H_{\text{phs2}} \quad (12)$$

235 These expressions in Figure 3 have been schematically represented and the definition of each term  
 236 in Table 3. Thus, the first term of the water heat balance  $\left((\overline{\Delta h_{fw}})^T \left(\tilde{E}_{w,w}^T \bar{p}_{w,w}\right)\right)$  refers to the heat  
 237 associated to the transformations that take place in the aqueous phase, namely, it encompasses the  
 238 heat of all transformations that occur in this phase. The second term  $\left((\overline{\Delta h_{fw}})^T \left(\tilde{E}_{w,g1}^T \bar{p}_{w,g1}\right)\right)$   
 239 provides the stoichiometric enthalpies of formation of the components present in the aqueous phase,  
 240 and the third term  $\left((\overline{\Delta h_{fg1}})^T \left(\tilde{E}_{g1,w}^T \bar{p}_{g1,w}\right)\right)$  the stoichiometric enthalpies of formation of the  
 241 components present in the first gaseous phase. Applying the first law of thermodynamics, the sum

242 of both terms refers to the water-gas/gas-water convective transferences, namely, the heat  
243 transferred due to the stripping/absorption and evaporation/condensation transferences. In such a  
244 transfer, besides heat production or consumption, an enthalpy associated to the matter is transferred  
245 between the phases, producing an increase in the net heat of the target phase, though not of the  
246 specific heat. In the model these terms have been defined as enthalpy inputs and outputs due to  
247 transformations, as can be seen in Table 3.

248

249 By way of simplification, for the aqueous flow heat estimation, only water enthalpy has been  
250 considered, ignoring the enthalpy of dissolved compounds that make up the aqueous phase. In the  
251 modelling of convective phenomenon, natural convection heat transfer on the phase surface  
252 depends on the contact surface, the temperature difference between the phases and also on the  
253 thermophysical properties of the phases involved (see Table 3). One of the most noticeable  
254 differences to be considered in open tank modelling is precisely this term. In closed tank modelling,  
255 natural convection is considered, whereas in open tank modelling with forced convection, this term  
256 can be highly influenced by wind velocity and temperature differences between the phases and the  
257 atmosphere.

258

#### 259 **4. VALIDATION OF THE METHODOLOGY FOR ESTIMATING** 260 **TRANSFORMATION HEAT ( $\Delta H_r^\circ$ )**

261 First validation of the proposed methodology has been focused on comparing the theoretical model-  
262 based heat values obtained with the E-PWM with other studies. Table 4 shows a comparison  
263 between the transformation heat values calculated with the proposed methodology and a set of  
264 values presented in bibliography, previously estimated both experimentally (E) or theoretically (T).  
265 In order to validate the methodology as rigorously as possible, some model reactions had to be  
266 modified (for example, some bibliographic reactions don't consider the biomass growth) to make  
267 more validation cases available.

268

269 It is interesting to note that the deviations with almost all reactions have been as low as 5%, with the  
270 exception of the enthalpy change of reaction estimated theoretically for the conversion of acetic  
271 acid to methane (reaction 7), where the discrepancies may be due to differences in the enthalpies of  
272 formation used for the products and/or reactants. Therefore, these comparative results confirm that  
273 the enthalpy change of reaction estimated by the Extended Plant-Wide modelling methodology is in  
274 accordance with the values traditionally estimated both theoretically and experimentally.

275

276 Despite numerous experimental studies published, there is no consensus on the determination of the  
277 specific heat yields (see Table 4), although it has been estimated an approximate range of 12–18 kJ  
278 gCOD<sup>-1</sup> removed. These discrepancies can be attributed to the heterogeneity in the samples'  
279 composition due to the diversity in the organic components present (Cooney *et al.*, 1968). It is also  
280 important to note that, although the enthalpy change of reaction values proposed in literature are  
281 attributed to the oxidation of organic materials, these experimental estimations implicitly include  
282 other smaller transformation heats like, for example, those associated with hydrolysis or CO<sub>2</sub>  
283 stripping. In order to show the additional information offered by the proposed E-PWM  
284 methodology, Table 5 first row presents the theoretical specific heat yields for the seven  
285 carbonaceous substrates included in the model under study, showing the small differences  
286 associated with substrate composition, but within the range proposed in literature. Additionally, the  
287 second row illustrates the expected changes in the theoretical heats when substrate oxidation and  
288 CO<sub>2</sub> stripping transformations are both considered in the calculations, demonstrating the relevance  
289 of taking into account all the simultaneous transformations. This fact can explain some of the  
290 discrepancies found in the experimental results presented in the literature.

291

292 Once the appropriate calculation of the specific heat yields has been validated, the applicability of

293 the proposed E-PWM methodology for the dynamic simulation of heat fluxes and temperature  
294 prediction has been analysed. For this, two illustrative examples have been constructed and  
295 implemented in the WEST simulation platform ([www.mikebydhi.com](http://www.mikebydhi.com)), for its subsequent analysis.

296

#### 297 **4.1. Example I: Analysis of dynamic heat exchanges in a WWTP biological reactor**

298 This first case study shows the usefulness of the E-PWM methodology for a detailed prediction of  
299 the dynamic evolution of the heat exchanges generated in the biological reactors of WWTPs. The  
300 simulation example corresponds to the water line of the BSM2 layout (Jeppsson *et al.*, 2007),  
301 maintaining its physical attributes and using the 365-day dynamic influent data file. The data of  
302 atmospheric temperature, solar radiation and wind velocity have been extracted from the Spanish  
303 National Meteorological Agency (<http://www.aemet.es>) corresponding to measurements made in  
304 northern Spain in 2012. Regarding the influent water temperature, the profile has been estimated  
305 from atmospheric data and previous year's tendencies in that area (every day of the year, the input  
306 water temperature is higher than the temperature of the atmosphere).

307

308 Figure 4a shows the predicted contribution of the most significant heat fluxes in the overall balance.  
309 The mild temperatures and abundant rainfall that characterized the oceanic climate means that the  
310 solar radiation flux ( $\Delta H$  radiation) and the conduction and convection fluxes ( $\Delta H$  cond/conv) do not  
311 have the significance that can be expected in other areas. Although surprised that the term of heat  
312 transfer due to aeration hasn't appeared in the figure 4a, this term in the  $\Delta H$  cond/conv term has  
313 been included along with the transfer between the atmosphere and the water phase. The aeration  
314 provide heat to the system but this heat is offset by losses due to contact between the atmosphere  
315 and the water.

316 Figure 4b shows a detailed description of the main heat fluxes within the reactors, differentiating  
317 between the heat supplied by the biological transformations and the heat consumed by evaporation

318 and stripping. Simulations results clearly show how the most significant heat fluxes are due to COD  
319 removal (denitrification in anoxic reactors and heterotrophic growth in aerobic reactors) and  
320 nitrification reactions. To a lesser extent, but also relevant is the stripping of CO<sub>2</sub> and evaporation.

321

322 Simulation results (not presented) have shown that the expected overall increase in the water  
323 temperature from influent to effluent ranges between 0.8 and 1.5 degrees depending on the  
324 radiation term, coinciding with the ranges previously published by la Cour Jansen *et al.* (1992) and  
325 Makinia *et al* (2005). The proposed E-PWM methodology facilitates a detailed description of the  
326 contribution of different transformations in the heat flows and temperature variations. For example,  
327 at this particular case-study, simulation results show that the nitrification and heterotrophic growth  
328 reactions increase the tank temperature 0.6-0.8 degrees while denitrification only by 0.23 degrees.

329 Evaporation and stripping reactions are widely influenced by atmospheric temperature, and  
330 decrease the temperature by 0.05-0.2 degrees. As expected, the effect of transformation heats in  
331 process temperature is not very relevant in conventional activated sludge reactors. However, it can  
332 be very significant in other processes that exhibit higher biological activity and lower heat transport  
333 with the environment like, for example, the Autothermal Thermophilic Aerobic Digesters (ATAD).

334

#### 335 **4.2. Example II: Analysis of the heat exchanges generated in an ATAD reactor**

336 The ATAD digesters exhibit a high organic matter oxidation, being able to maintain thermophilic  
337 conditions without the external addition of heat (except recirculations/mixing energy). To analyse  
338 the predictive capacity of the methodology applied to an ATAD reactor, the first step has been the  
339 comparison between the simulation results and the experimental data obtained in the full scale  
340 ATAD at the Tudela WWTP (de Garcia *et al.*, 2009; Gomez *et al.*, 2007). This ATAD digester is a  
341 completely stirred tank reactor with a total effective volume of 350 m<sup>3</sup>. In the analysed 14-day  
342 period, the digester operated at 10 days hydraulic retention time with discontinuous charges and

343 discharges of the reactor every 24h. A period with abrupt changes in the organic loading rate (OLR)  
344 was selected for the validation of the thermal model under both oxygen limiting and substrate  
345 limiting conditions. To achieve these two conditions, the aeration flow rate of  $9,200 \text{ m}^3 \text{ d}^{-1}$   
346 remained constant, gradually increasing the OLR (see Table 6). A detailed description of the  
347 stoichiometric, kinetic and physico-chemical parameters can be found in de Gracia *et al.* (2009).

348

349 The dynamic results obtained in the simulation are shown in Figure 5a, where the experimental and  
350 simulated aqueous phase temperatures obtained in the selected period are compared, obtaining a  
351 proper fit both in terms of substrate limiting conditions (days 0 to 9) and oxygen limiting conditions  
352 (days 9 to 14). The evolution of temperature in oxygen limiting conditions makes possible the  
353 calibration of the oxygen transfer coefficient ( $k_{La}$ ), whereas temperature data under substrate  
354 limiting conditions supplies the information required for calibrating the heat flux associated with  
355 aeration.

356

357 By analysing the thermal flux of the system (Figure 5b), it can be seen that biological processes  
358 ( $\Delta H_r$  water) are the most important heat flux contributors, representing 60-70% of the heat in the  
359 process. The contour of this flux area shows the evolution of organic matter oxidation, clearly  
360 differentiating substrate limiting and oxygen limiting areas. The heat dissipated due to the liquid  
361 and gas phase transformations ( $\Delta H_r$  water-gas) is the second most important heat flux, representing  
362 15-30% of the heat in the process. Of this percentage, 10% corresponds to  $\text{CO}_2$  stripping, and the  
363 remaining 90% to the heat lost by evaporation. In this example, atmospheric and solar radiation  
364 have not been graphed since they were negligible compared to other terms.

365

366 The proposed E-PWM methodology also makes possible a detailed dynamic analysis of the  
367 different terms in heat generation and transport as a function of the influent load or operational

368 strategies. Next examples briefly show the effect of ventilation and the substrate fed in the ATAD  
369 temperature.

370

#### 371 **4.2.1. Model-based exploration of the effect of air flow in an ATAD digester**

372 Aeration is a key factor in aerobic digestion from the point of view of biological reaction and heat  
373 balance. If the process is working with oxygen concentrations under the stoichiometric value  
374 (oxygen limiting conditions), the oxygen transfer will mark the substrate consumption rate of the  
375 system and therefore the sludge heating (Messenger *et al.*, 1990). Thus, the digester temperature can  
376 be controlled with the air flow, until the substrate is exhausted or the stoichiometric oxygen value is  
377 reached. Conversely, if the system is working with oxygen concentrations over the stoichiometric  
378 (substrate limiting conditions), the heating degree will depend on the amount of substrate fed. In  
379 contrast to oxygen limiting conditions, an excess of aeration can cause digester cooling due to the  
380 temperature gradient of the bubbles and the liquid phase.

381

382 The model's ability to identify these ventilation effects is essential for an appropriate selection of  
383 the operational conditions. Still, it is important to mention that for a correct prediction of the heat of  
384 reaction, it is necessary to estimate experimentally the respiration quotient, especially important  
385 when the system is working under substrate limiting conditions. Figure 6 shows an exploration of  
386 the expected reactor temperature of the Tudela ATAD for the same OLR of  $4.0 \text{ Kg COD}\cdot\text{m}^{-3} \text{ d}^{-1}$   
387 under different aeration flows. It can be clearly observed how excess air can cause a cooling of the  
388 aqueous phase, decreasing the temperature to values obtained with oxygen limiting conditions, with  
389 the disadvantage of having higher costs. Model-based exploration can facilitate the selection of the  
390 most appropriate aeration flow. The proposed E-PWM methodology is already prepared for dealing  
391 with different gas phases, making possible the simulation of pure oxygen supply.

392

#### 393 **4.2.2. Model-based exploration of the effect of influent characterization in an ATAD digester**

394 Different studies (Heijnen, 1999; Heidrich *et al.*, 2011; Hill *et al.*, 2012) have shown that oxidation  
395 heat is closely related to the composition of the feed. In this section, the effect of a change in the  
396 composition of the sludge fed in the liquid phase has been explored by simulation, using the E-  
397 PWM methodology. Table 7 shows the three influent characterisations used for the model-based  
398 exploration.

399  
400 Figure 7a shows the predicted evolution of process temperature for the three load characterisations.  
401 The rise in the concentration of carbohydrates has led to an increase in liquid temperature of 0.4 °C  
402 for this specific OLR (a decrease of 0.4 °C for Characterisation 2). This temperature variation  
403 would have been greater using a higher OLR or energy crops such as maize grains, artichoke or  
404 wheat, among others.

405  
406 The enthalpy change of reaction of each characterisation is plotted in Figure 7b showing the  
407 capacity of E-PWM methodology for exploring the effect of influent characterisation in  
408 temperature. As expected the greatest heat are obtained for the influent rich in carbohydrates. It is  
409 interesting to note that the global transformations heat and, consequently the specific heat yield, is  
410 varying in time, depending on the evolution of substrate fractioning within the reactor.

## 411 412 **5. CONCLUSIONS**

413 The paper presents a new methodology, based on the well-known Hess's law, for the rigorous and  
414 systematic calculation of heat balances in biochemical reactors. Starting from a complete  
415 description of model components stoichiometry and enthalpies of formation, the proposed  
416 modelling methodology, called Extended Plant-Wide Modelling (E-PWM), has integrated  
417 successfully the simultaneous calculation of both the conventional mass balances and the heat

418 balances in an expandable multi-phase matrix structure, which facilitates a detailed prediction of the  
419 main heat fluxes in the biochemical reactors. Without wanting to focus on the mere calculation of  
420 heat exchanges in a single reactor, the heat balance has been also integrated into the CEIT Plant-  
421 Wide Modelling methodology (Grau *et al*, 2007) in order to conduct a comprehensive analysis of  
422 entire WWTPs.

423

424 The transformation heats and specific heat yields estimated with the proposed methodology have  
425 been successfully contrasted with other experimental or theoretical studies previously presented in  
426 the literature. Additionally, the E-PWM offers very comprehensive information about the different  
427 heat fluxes associated with each particular reaction or transport, facilitating, for example, an  
428 exhaustive analysis of the effect of operational conditions or influent fractioning in temperature  
429 evolution. Finally, it is interesting to remark that the proposed heat transfer modelling methodology  
430 can be easily incorporated to the existing WWTPs simulators that are based on a detailed  
431 description of model components and transformations like, for example, those based on the PWM  
432 methodology.

433

#### 434 **ACKNOWLEDGEMENTS**

435 The authors would like to thank the financial support from the Spanish Ministry of Science and  
436 Innovation (NOVEDAR\_Consolider CDS2007-00055).

437

#### 438 **References**

- 439 Adriaanse, N., Dekker, H., Coops, J., 1965. Heats of combustion of normal saturated fatty acids and  
440 their methyl esters, *Rec. Trav. Chim. Pays/Bas*, 84, 393-407.
- 441 Andrews J.F., Kambhu K., 1969. Aerobic thermophilic process for the biological treatment of  
442 wastes – simulation studies. *J Water Pollut. Control Fed.* 41. 127-141.

- 443 Argaman, Y., Adams, C.E. Jr., 1977. Comprehensive temperature model for aerated biological  
444 systems. *Prog. Water Technol.* 9(2), 397–409.
- 445 Brown, R.C., 2011. *Thermochemical processing of Biomass: Conversion into fuels, chemicals and*  
446 *power.* Wiley, United Kingdom.
- 447 Brown, T.L., LeMay, H.E. Jr, Bursten, B.E., 1993. *Química. La ciencia central.* McGraw-Hill, Ed.5,  
448 USA.
- 449 Buttiglieri, G., Bouju, H., Malpei, F., Ficara, E., Canziani, R., 2010. Microcalorimetry: A tool to  
450 investigate aerobic, anoxic and anaerobic autotrophic and heterotrophic biodegradation.  
451 *Biochemical Engineering Journal*, 52(1), 25-32.
- 452 Chang R., 1999. *Química*, Ed 6, McGraw-Hill, México.
- 453 Constantinou, L., Gani, R., 1994. New Group Contribution Method for Estimating Properties of  
454 Pure Compounds, *AIChE J.*, 40(10), 1697-1710.
- 455 Cooney, C.L., Wang, D.I.C., Mateles, R.I., 1968. Measurement of Heat Evolution and Correlation  
456 with Oxygen Consumption during Microbial Growth. *Biotech. & Bioengineering*, XI, 269-281.
- 457 Copp, J.B., Jeppsson, U., Rosen, C., 2003. Towards an ASM1-ADM1 State Variable Interface for  
458 Plant-Wide Wastewater Treatment Modeling. In: *Proceedings of the WEFTEC, Los Angeles*  
459 *Convention Center, Los Angeles, CA, USA, October 11-15.*
- 460 Daigger, G.T., 2011. A practitioner's perspective on the uses and future developments for  
461 wastewater treatment modelling. *Water Science & Technology* 63 (3), 516.
- 462 Daverio, E., Aulenta, F., Ligthart, J., Bassani, C., Rozzi, A., 2003. Application of calorimetric  
463 measurements for biokinetic characterisation of nitrifying population in activated sludge. *Water*  
464 *Research*, 37(11), 2723-2731.
- 465 de Gracia, M., Grau, P., Huete, E., Gómez, J., García-Heras, J.L., Ayesa, E., 2009. New generic  
466 mathematical model for WWTP sludge digesters operating under aerobic and anaerobic  
467 conditions: Model building and experimental verification. *Water Research*, 43(18), 4626-4642.

- 468 de Gracia M., Sancho L., García-Heras J.L., Vanrolleghem P.A., Ayesa E., 2006. Mass and Charge  
469 Conservation Check in Dynamic Models: Application to the New ADM1 Model. *Water Science  
470 & Technology*, **53**(1), 225-240.
- 471 Everett, D.H., Wynne-Jones, F.K., 1939. The thermodynamics of acid-base equilibria. Transaction  
472 of the Faraday Society. 35, 1380-1401
- 473 Freedman, B., Bagby, M.O., Khoury, H., 1989. Correlation of heats of combustion with empirical  
474 formulas for fatty alcohols, *J. Am. Oil Chem. Soc.*, 66, 595-596.
- 475 Gallert, C., Winter, J., 2005. Bacterial Metabolism in Wastewater Treatment Systems. In:  
476 Jördening, H.J., Winter, J. (Eds.), *Environmental Biotechnology – Concepts and Applications*.  
477 Wiley-VCH, Weinheim. 1-48.
- 478 Gómez, J., de Gracia, M., Ayesa, E., de las Heras, J.L., 2007. Mathematical modelling of  
479 autothermal thermophilic aerobic digesters. *Water Research*, 41, 959-968.
- 480 Grau, P., de Gracia, M., Vanrolleghem, P., Ayesa, E., 2007. A new Plant-Wide modelling  
481 methodology for WWTPs. *Water Research*, 41(19), 4357-4372.
- 482 Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D.A., Rand, M.H., 2003.  
483 Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and  
484 Technetium. Elsevier Science, Amsterdam.
- 485 Gillot, S., Vanrolleghem, P.A., 2003. Equilibrium temperature in aerated basins-comparison of two  
486 prediction models. *Water Research* 37, 3742-3748.
- 487 Heidrich, E.S., Curtis, T.P., Dolfing, J., 2011. Determination of the Internal Chemical Energy of  
488 Wastewater. *Environ. Sci. Technology*. 45, 827-832.
- 489 Heijnen, J.J., 1999. Bioenergetics of Microbial Growth. In: Flickinger, M.C. & Drew, S.W. (eds)  
490 *Encyclopedia of Bioprocess Technology: Fermentation, Biocatalysis, and Bioseparation*. Wiley-  
491 Interscience, New York, pp. 267–291.
- 492 Heinritz B., Gehrhardt M., Baumann F., Rogge G., Hedlich R., Ringpfeil M., 1990. Biomass

- 493 production by thermophilic microorganisms simultaneously using reaction heat. *J. Chem. Tech.*  
494 *Biotechnol.* 49, 285-295.
- 495 Henze, M., Gujer, W., Mino, T., Van Loosdrecht, M.C.M., 2000. Activated Sludge Models ASM1,  
496 ASM2, ASM2d and ASM3. Scientific and Technical Report N°9, IWA Publishing, London.
- 497 Hill, R.W., Wyse, G.A., Anderson, M., 2012. *Animal Physiology*. Sinauer Associates Inc., Ed.3,  
498 Sunderland, MA.
- 499 Hukkerikar, A.S., Meier, R., Sin, Gürkan, Gani, R., 2013. A method to estimate the enthalpy of  
500 formation of organic compounds with chemical accuracy. *Fluid Phase Equilibria Volume*  
501 348(25), 23-32.
- 502 Inoije, S., Sawayama, S., Ogi, T., Yokoyama, S.Y., 1996. Organic Composition of Liquidized  
503 Sewage Sludge. *Biomass and Bioenergy*. 10, 37–40. Jeppsson U., Pons M.N., Nopens I., Alex J.,  
504 Copp J.B., Gerneay K.V., Rosen C., Steyer J.P., Vanrolleghem P.A., 2007. Benchmark  
505 simulation model No 2 – general protocol and exploratory case studies. *Wat. Sci. Tech.*, 53(8),  
506 67-78.
- 507 Jewell W.J., 1982. Autoheated Aerobic Thermophilic Digestion with Air Aeration. EPA project No.  
508 R 804636, MERL Report, NTIS PB-82-196908.
- 509 la Cour Jansen, J., Kristensen, G.H., Laursen, K.D., 1992. Activated sludge nitrification in  
510 temperate climate. *Water Sci. Technol.* 25(4–5), 177–184.
- 511 Lapara, T.M., Alleman, J.E., 1999. Thermophilic aerobic biological wastewater treatment. *Water*  
512 *Research*, 33(4), 895-908.
- 513 Lebedeva, N.D., 1964. Heats of combustion of monocarboxylic acids, *Russ. J. Phys. Chem.* (Engl.  
514 Transl.), 38, 1435-1437.
- 515 Lippi, S., Rosso, D., Lubello, C., Canziani, R., Strenstrom, M., 2009. Temperature modelling and  
516 prediction for activated sludge systems. *Water Science and Technology* 59, pp 125-131.
- 517 Makinia, J., Scott, A., Zima, P., 2005. Temperature modeling in activated sludge systems - A case

- 518 study. *Water Environ. Res.* 77, 525–532.
- 519 Masterton, W.L., Hurley, C.N., 2003. *Química. Principios y Reacciones*. Ediciones Paraninfo, Ed 4.  
520 Madrid.
- 521 McCarty P.L., 1972. *Energetics of organic matter degradation*. *Water Pollution Microbiology*, R.  
522 Mitchell Ed., Wiley-Interscience, NY.
- 523 Messenger, J.R., Ekama, G.A., 1993. Evaluation of the dual digestion system: Part 4 - Simulation  
524 of the temperature profile in the batch fed aerobic reactor. *Water SA*, 19(3) 209-215.
- 525 Messenger, J.R., Ekama, G.A., de Villiers, H.A., Kenmuir, K., Laubscher, S.A., 1992. Evaluation  
526 and optimisation of dual digestion of sewage sludge – Part 2: Aerobic reactor performance.  
527 Final report WRC 189/3/92. Water Research Commission, PO Box 824. Pretoric, 0001.
- 528 Messenger, J.R., de Villiers, H.A., Ekama, G.A., 1990. Oxygen utilization rate as a control  
529 parameter for the aerobic stage in dual digestion. *Wat. Sci. Tech.*, 22(12) 217-227.
- 530 Metcalf & Eddy., 2004. *Wastewater Engineering, Treatment Disposal and. Reuse*, 4th Edition.  
531 Singapore, Mcgraw-Hill. Mosely, F.E., and Hughes, D.A. 1975.
- 532 National Institute of Standards and Technology, NIST. <http://www.nist.gov>
- 533 Nelson, L.D., Cox, M.M., 2005. *Lehninger, Principles of biochemistry*. N. H. Freeman, Ed. 4, New  
534 York.
- 535 Novotny, V., Krenkel, P. 1973. Evaporation and heat balance in aerated basins. *AIChE Symp.*  
536 *Series, Water* 70(136), 150–159.
- 537 Oh, S.T., Martin, A.D., 2010. Long chain fatty acids degradation in anaerobic digester:  
538 Thermodynamic equilibrium consideration. *Process Biochemistry*. 45(3): 335-345.
- 539 Oh, S.T., Martin, A.D., 2007. Thermodynamic Equilibrium Model in anaerobic digestion process.  
540 *Biochemical Engineering Journal*. 34(3): 256-266.
- 541 Paul, P., 2013. Assessing the influence of pronounced diurnal temperature variations in  
542 nontemperate zones on the denitrification/nitrification rate using the COST Benchmark

- 543 activated sludge model no. 1 simulation. *Water and Environmental Journal*. Print ISSN 1747-  
544 6585.
- 545 Perry, R.H., Green, D.W., 1999. Perry's "Chemical Engineer's Handbook", McGraw-Hill, USA.
- 546 Pitt, A.J., Ekama, G.A., 1996. Dual digestion of sewage sludge with air and pure oxygen. *Procs 69<sup>th</sup>*  
547 *Water Environment Federation Annual conference and exhibition, Dallas TX, 2, 69-82.*
- 548 Pitt, A.J., Ekama, G.A., 1995. The dual digestion of sewage sludge using air and pure oxygen. UCT  
549 Report No 87/1995, Dept. of Eng., Univ. of Cape Town, Rondebosch, Cape, RSA.
- 550 Prochazka, G.J., Payne, W.J., Mayberry, W.R., 1973. Calorific Contents of Microorganisms.  
551 *Biotechnology and Bioengineering, Vol.XV, 1007-1010.*
- 552 Reger, D.L., Goode, S.L., Ball, D.W., 2010. *Chemistry: Principles and Practice. Ed. 3. Chemistry*  
553 *Department Books. Bedford. CA.*
- 554 Reichert, P., Borchardt D., Henze M., Rauch W., Shanahan P., Somlyódy L. and Vanrolleghem P.,  
555 2001. *River Water Quality Model N°1. Scientific and Technical Report N°12, IWA Publishing,*  
556 *London.*
- 557 Riley, D.W., and Forster, C.F., 2002. An evaluation of an autothermal aerobic digestion system.  
558 *Transactions of the Institution of Chemical Engineers, Part B - Process Safety and Env.*  
559 *Protection, 80B . pp. 100-104.* Sethi, G., Kumar, D., Sarna, J., Maurya, L., Ram, R.B., 2011.  
560 *Future of water treatment: Membrane bioreactor technology. IPPTA J. 4, 145-149.*
- 561 Sedory, P.E., Stenstrom, M.K., 1995. Dynamic prediction of wastewater aeration basin temperature.  
562 *Journal of Environmental Engineering. 121, 609-618.*
- 563 Shizas, I., Bagley, D.M., 2004. Experimental Determination of Energy Content of Unknown  
564 *Organics in Municipal wastewater Streams. Journal of Energy Engineering. 130(2):45-53.*
- 565 Steele, W.V., Chirico, R.D., Cowell, A.B., Knipmeyer, S.E., Nguyen, A., 1997. Thermodynamic  
566 *properties and ideal-gas enthalpies of formation for 2-aminoisobutyric acid (2-methylalanine),*  
567 *acetic acid, (4-methyl-3-penten-2-one), 4-methylpent-1-ene, 2,2'-bis(phenylthio)propane, and*

- 568 glycidyl phenyl ether (1,2-epoxy-3-phenoxypropane). J. Chem. Eng. Data, 42, 1052-1066.
- 569 van Hulle, S.W.H., vandeweyer, H.J.P., Meesschaert, B.D., Vanrollegheem, P.A., Dejans, P.,
- 570 Dumoulin, A., 2010. Engineering aspects and practical application of autotrophic nitrogen
- 571 removal from nitrogen rich streams, Chem. Eng. J., 162, 1–20.
- 572 Vismara, R., 1985. A model for autothermic aerobic digestion. Wat. Res. 19, 441-447.
- 573 Zanoni, A.E., Mueller, D.L., 1982. Calorific value of wastewater plant sludge. J. Environ. Eng. Div.
- 574 (Am. Soc. Civ. Eng.). 108(1), 187-195.

**Table 1** - Gas phase formation enthalpies

i	Name	Formula	Description	$\Delta h_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta h_f^\circ$ (kJ g <sub>stoich. unit</sub> <sup>-1</sup> )	Reference
1	G <sub>CO2</sub>	CO <sub>2</sub>	Carbon dioxide	-393.51	-32.79 kJ g <sub>C</sub> <sup>-1</sup>	Perry & Green (1999)
2	G <sub>H2</sub>	H <sub>2</sub>	Hydrogen	0.00	0.00 kJ g <sub>COD</sub> <sup>-1</sup>	Perry & Green (1999)
3	G <sub>CH4</sub>	CH <sub>4</sub>	Methane	-74.80	-1.17 kJ g <sub>COD</sub> <sup>-1</sup>	Perry & Green (1999)
4	G <sub>NH3</sub>	NH <sub>3</sub>	Ammonia	-45.90	-3.28 kJ g <sub>N</sub> <sup>-1</sup>	Perry & Green (1999)
5	G <sub>N2</sub>	N <sub>2</sub>	Nitrogen	0.00	0.00 kJ g <sub>N</sub> <sup>-1</sup>	Perry & Green (1999)
6	G <sub>O2</sub>	O <sub>2</sub>	Oxygen	0.00	0.00 kJ g <sub>O2</sub> <sup>-1</sup>	Perry & Green (1999)
7	G <sub>H2O</sub>	H <sub>2</sub> O	Water steam	-241.81	-13.43 kJ g <sub>H2O</sub> <sup>-1</sup>	Perry & Green (1999)

Table 2 - Water phase formation enthalpies

i	Name	Formula	Description	$\Delta h_f^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta h_f^{\circ}$ (kJ g <sub>stoich</sub> <sup>-1</sup> )	Reference
1	S <sub>H2O</sub>	H <sub>2</sub> O	Water steam	-285.84	-15.88 kJ g <sub>H2O</sub> <sup>-1</sup>	Perry & Green (1999)
2	S <sub>O2</sub>	O <sub>2</sub>	Dissolved Oxygen	0.00	0.00 kJ g <sub>O2</sub> <sup>-1</sup>	Perry & Green (1999)
3	S <sub>H<sup>+</sup></sub>	H <sup>+</sup>	Protons	0.00	0.00 kJ g <sub>H</sub> <sup>-1</sup>	Brown <i>et al.</i> (1993)
4	S <sub>OH<sup>-</sup></sub>	OH <sup>-</sup>	Hydroxide ions	-230.00	-230.00 kJ g <sub>H</sub> <sup>-1</sup>	Brown <i>et al.</i> (1993)
5	S <sub>HPO4=</sub>	(HPO <sub>4</sub> ) <sup>=</sup>	Hydroxy phosphate	-1298.70	-41.89 kJ g <sub>P</sub> <sup>-1</sup>	Chang (1999)
6	S <sub>H2PO4-</sub>	(H <sub>2</sub> PO <sub>4</sub> ) <sup>-</sup>	Dihydroxy	-1302.48	-42.01 kJ g <sub>P</sub> <sup>-1</sup>	Chang (1999)
7	S <sub>NH4+</sub>	(NH <sub>4</sub> ) <sup>+</sup>	Ammonium	-132.50	-9.46 kJ g <sub>N</sub> <sup>-1</sup>	Brown <i>et al.</i> (1993)
8	S <sub>NH3</sub>	NH <sub>3</sub>	Ammonia	-80.29	-5.73 kJ g <sub>N</sub> <sup>-1</sup>	Brown <i>et al.</i> (1993)
9	S <sub>CO2</sub>	CO <sub>2</sub>	Dis. Carbon dioxide	-412.90	-34.41 kJ g <sub>C</sub> <sup>-1</sup>	Chang (1999)
10	S <sub>HCO3-</sub>	(HCO <sub>3</sub> ) <sup>-</sup>	Bicarbonate	-691.10	-57.59 kJ g <sub>C</sub> <sup>-1</sup>	Chang (1999)
11	S <sub>SU</sub>	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	Monosaccharides	-1268.20	-6.61 kJ g <sub>COD</sub> <sup>-1</sup>	Reger <i>et al.</i> (2010)
12	S <sub>AA</sub>	C <sub>4</sub> H <sub>6.10</sub> O <sub>1.2N</sub>	Amino acids	-306.10	-2.29 kJ g <sub>COD</sub> <sup>-1</sup>	NIST
13	S <sub>FA</sub>	C <sub>16</sub> O <sub>2</sub> H <sub>32</sub>	LCFAs	-848.40	-1.15 kJ g <sub>COD</sub> <sup>-1</sup>	Lebedeva (1964)
14	S <sub>HVA</sub>	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Valeric acid	-558.90	-2.69 kJ g <sub>COD</sub> <sup>-1</sup>	Adriaanse <i>et al.</i> (1965)
15	S <sub>VA-</sub>	C <sub>5</sub> H <sub>9</sub> O <sub>2</sub> <sup>-</sup>	Valerate	<del>-501.07</del>	<del>-2.4128</del> kJ g <sub>COD</sub> <sup>-1</sup>	<del>Constantinou <i>et al.</i> (1994)</del> Hukkerikar <i>et al.</i> , 2013
16	S <sub>HBU</sub>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Butyric acid	-533.92	-3.34 kJ g <sub>COD</sub> <sup>-1</sup>	Lebedeva (1964)
17	S <sub>BU-</sub>	C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> <sup>-</sup>	Butyrate	-519.20	-3.25 kJ g <sub>COD</sub> <sup>-1</sup>	Everett <i>et al.</i> (1939)
18	S <sub>HPRO</sub>	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propionic acid	-510.80	-4.56 kJ g <sub>COD</sub> <sup>-1</sup>	Lebedeva (1964)
19	S <sub>PRO-</sub>	C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup>	Propionate	-507.79	-4.53 kJ g <sub>COD</sub> <sup>-1</sup>	Everett <i>et al.</i> (1939)
20	S <sub>HAC</sub>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid	-483.52	-7.56 kJ g <sub>COD</sub> <sup>-1</sup>	Steele <i>et al.</i> (1997)
21	S <sub>AC-</sub>	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	Acetate	-482.09	-7.53 kJ g <sub>COD</sub> <sup>-1</sup>	Everett <i>et al.</i> (1939)
22	S <sub>H2</sub>	H <sub>2</sub>	Hydrogen	0.00	0.00 kJ g <sub>COD</sub> <sup>-1</sup>	Perry & Green (1999)
23	S <sub>CH4</sub>	CH <sub>4</sub>	Dis. Methane	-82.97	-1.30 kJ g <sub>COD</sub> <sup>-1</sup>	NIST
24	S <sub>N2</sub>	N <sub>2</sub>	Dis. Nitrogen	0.00	0.00 kJ g <sub>N</sub> <sup>-1</sup>	Perry & Green (1999)
25	S <sub>NO2-</sub>	NO <sub>2</sub> <sup>-</sup>	Nitrites	-104.60	-7.47 kJ g <sub>N</sub> <sup>-1</sup>	Masterton & Hurley (2003)
26	S <sub>HNO2</sub>	HNO <sub>2</sub>	Nitrous acid	-116.00	-8.29 kJ g <sub>N</sub> <sup>-1</sup>	Guillaumont <i>et al.</i> (2003)
27	S <sub>NO3-</sub>	(NO <sub>3</sub> ) <sup>-</sup>	Nitrates	-206.57	-14.76 kJ g <sub>N</sub> <sup>-1</sup>	Chang (1999)
28	S <sub>I</sub>	C <sub>7</sub> H <sub>9.1</sub> O <sub>2.65</sub> NP <sub>0.05</sub>	Soluble Inerts	-495.00	-1.34 kJ g <sub>COD</sub> <sup>-1</sup>	Need estimation
29	S <sub>P</sub>	C <sub>7</sub> H <sub>9.1</sub> O <sub>2.65</sub> NP <sub>0.05</sub>	Lysis sol. Product	-495.00	-1.34 kJ g <sub>COD</sub> <sup>-1</sup>	Need estimation
30	X <sub>C1</sub>	C <sub>13.7</sub> H <sub>24</sub> O <sub>3.8</sub> N <sub>0.5</sub> P <sub>0.035</sub>	Composites	-555.90	-1.94 kJ g <sub>COD</sub> <sup>-1</sup>	Need estimation
31	X <sub>C2</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Decay complex	-414.02	-2.54 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
32	X <sub>CH</sub>	C <sub>6</sub> H <sub>9.95</sub> O <sub>5</sub> P <sub>0.05</sub>	Carbohydrates	-979.00	-5.06 kJ g <sub>COD</sub> <sup>-1</sup>	Brown (2011)
33	X <sub>PR</sub>	(C <sub>4</sub> H <sub>6.1</sub> O <sub>1.2</sub> N) <sub>x</sub>	Proteins	-284.10	-2.13 kJ g <sub>COD</sub> <sup>-1</sup>	Nelson <i>et al.</i> , (2005)
34	X <sub>LI</sub>	C <sub>51</sub> H <sub>97.9</sub> O <sub>6</sub> P <sub>0.1</sub>	Lipids	-2474.17	-1.06 kJ g <sub>COD</sub> <sup>-1</sup>	Freedman <i>et al.</i> (1989)
35	X <sub>H</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Heterotrophic bac.	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
36	X <sub>AOB</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Nitrosomona bac.	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
37	X <sub>NOB</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Nitrobacter bac.	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
38	X <sub>SU</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Sugar degrader bac.	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
39	X <sub>AA</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Amino-acid	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
40	X <sub>FA</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	LCFA degrader bac.	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
41	X <sub>C4</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Val/but degrader	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
42	X <sub>PRO</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Propionate degrader	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
43	X <sub>AC</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Acetate degrader	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
44	X <sub>H2</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Hydrogen degrader	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
45	X <sub>AN</sub>	C <sub>5</sub> H <sub>6.9</sub> O <sub>2</sub> NP <sub>0.1</sub>	Anammox bac.	-414.02	-2.537 kJ g <sub>COD</sub> <sup>-1</sup>	Prochazka <i>et al.</i> (1973)
46	X <sub>I</sub>	C <sub>7</sub> H <sub>9.1</sub> O <sub>2.65</sub> NP <sub>0.05</sub>	Particulate inert	-718.41	-3.11 kJ g <sub>COD</sub> <sup>-1</sup>	Need estimation
47	X <sub>P</sub>	C <sub>7</sub> H <sub>9.1</sub> O <sub>2.65</sub> NP <sub>0.05</sub>	Lysis particulate	-718.41	-3.11 kJ g <sub>COD</sub> <sup>-1</sup>	Need estimation

Formatted Table

Formatted: Line spacing: single

Formatted: Font: Italic

48	X <sub>II</sub>	X	Inorganic inert	-	-	-
----	-----------------	---	-----------------	---	---	---

ACCEPTED MANUSCRIPT

**Table 3 - Variables, parameters and expressions used in the energy balance of a C-CSTR**

	Term	Description	Equations
Input / Output due to Transformations	$\bar{H}_{g1,g2}$	Enthalpy lost/gained by the 1 <sup>st</sup> gaseous phase due to transformation (from/to the 2 <sup>nd</sup> gaseous phase)	$(\bar{E}_{g1,g2}^T \bar{p}_{g1,g2})_i [(Cp_{g1})_i (T_{g1} - (T_{g1,ref})_i) + (h_{g1,ref})_i]$
	$\bar{H}_{g1,w}$	Enthalpy lost/gained by the 1 <sup>st</sup> gaseous phase due to transformation (from/to the aqueous phase)	$(\bar{E}_{g1,w}^T \bar{p}_{g1,w})_i [(Cp_{g1})_i (T_{g1} - (T_{g1,ref})_i) + (h_{g1,ref})_i]$
	$\bar{H}_{g2,g1}$	Enthalpy lost/gained by the 2 <sup>nd</sup> gaseous phase due to transformation (from/to the 1 <sup>st</sup> gaseous phase)	$(\bar{E}_{g2,g1}^T \bar{p}_{g2,g1})_i [(Cp_{g2})_i (T_{g2} - (T_{g2,ref})_i) + (h_{g2,ref})_i]$
	$\bar{H}_{g2,w}$	Enthalpy lost/gained by the 2 <sup>nd</sup> gaseous phase due to transformation (from/to the aqueous phase)	$(\bar{E}_{g2,w}^T \bar{p}_{g2,w})_i [(Cp_{g2})_i (T_{g2} - (T_{g2,ref})_i) + (h_{g2,ref})_i]$
Input	$H_{w,g1}$	Enthalpy lost/gained by the aqueous phase due to transformation (from/to the 1 <sup>st</sup> gaseous phase)	$(\bar{E}_{w,g1}^T \bar{p}_{w,g1})_{H_2O} [Cp_{w,H_2O} (T_w - T_{w,ref,H_2O}) + h_{w,ref,H_2O}]$
	$H_{w,g2}$	Enthalpy lost/gained by the aqueous phase due to transformation (from/to the 2 <sup>nd</sup> gaseous phase)	$(\bar{E}_{w,g2}^T \bar{p}_{w,g2})_{H_2O} [Cp_{w,H_2O} (T_w - T_{w,ref,H_2O}) + h_{w,ref,H_2O}]$
Output	$H_{w,in}$	Enthalpy associated with the aqueous influent	$[Cp_{w,H_2O} (T_{w,in} - T_{w,ref,H_2O}) + h_{w,ref,H_2O}] (\dot{m}_{w,in})_{H_2O}$
	$\bar{H}_{g,in}$	Enthalpy associated with the gaseous influent	$[(Cp_{g2})_i (T_{g2,in} - (T_{g2,ref})_i) + (h_{g2,ref})_i] (\dot{m}_{g,in})_i$
	$H_{w,out}$	Enthalpy associated with the aqueous effluent	$[Cp_{w,H_2O} (T_w - T_{w,ref,H_2O}) + h_{w,ref,H_2O}] (\dot{m}_{w,out})_{H_2O}$
Conduction / Convection	$\bar{H}_{g,out}$	Enthalpy associated with the gaseous effluent	$[(Cp_{g1})_i (T_{g1} - (T_{g1,ref})_i) + (h_{g1,ref})_i] (\dot{m}_{g,out})_i$
	$H_{phs1}$	Enthalpy flow transfer between the water and the 1 <sup>st</sup> gaseous phase	$\frac{\alpha_{phs,g1} (Gr Pr)^{n_{phs,g1}} (\bar{k}_{g1} \bar{X}_{g1}^T) (T_w - T_{g1}) A_{tank}}{\delta}$
	$H_{phs2}$	Enthalpy flow transfer between the water and the 2 <sup>nd</sup> gaseous phase	$\frac{\alpha_{phs,g2} (Gr Pr)^{n_{phs,g2}} (\bar{k}_{g2} \bar{X}_{g2}^T) (T_w - T_{g2}) A_{bubbles}}{\delta}$
Radiation	$H_{gc,out}$	Enthalpy lost/gained through walls and pipes by conduction (gaseous phase)	$k_{wls} (T_w - T_{atm}) A_w$
	$H_{wc,out}$	Enthalpy lost/gained through walls and pipes by conduction (aqueous phase)	$k_{wls} (T_{g1} - T_{atm}) A_g$
	$H_{atm,rad,g}$	Longwave atmospheric radiation flux (gaseous phase)	$k_{SB} A_g [\epsilon_{atm} (T_{g1}^*)^4 - (1 - \lambda_{atm}) \beta_{air} (T_{atm}^*)^4]$
	$H_{atm,rad,w}$	Longwave atmospheric radiation flux (aqueous phase)	$k_{SB} A_w [\epsilon_{atm} (T_w^*)^4 - (1 - \lambda_{atm}) \beta_{air} (T_{atm}^*)^4]$
Actuator	$H_{sol,rad,g}$	Shortwave solar radiation flux (gaseous phase)	$\alpha_{rad} k_{sol,rad} A_g$
	$H_{sol,rad,w}$	Shortwave solar radiation flux (aqueous phase)	$\alpha_{rad} k_{sol,rad} A_w$
	$H_{m,in}$	Enthalpy transmitted from the actuators (mechanical)	$P_m (1 - \eta_m)$

where,

$$Gr = \frac{g \beta_{phs} (T_w - T_{med}) \delta^3}{(\bar{u}_{med} \bar{X}_{med}^T)^2}$$

$$Pr = \frac{(\bar{\mu}_{med} \bar{X}_{med}^T) (\bar{Cp}_{med} \bar{X}_{med}^T)}{(\bar{k}_{med} \bar{X}_{med}^T)}$$

**Table 4** – Comparison of transformation heat estimated in modelling with experimental and theoretical literature data

Reaction	$\Delta h_r^\circ$		Reference
	Model	Literature	
1 Substrate (aq.) + xO <sub>2</sub> (g) → yH <sub>2</sub> O(l) + zCO <sub>2</sub> (g)+Biomass		12.28 – 16.46 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 13.32 – 15.12 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 14.30 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 13.5 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 12.50 – 16.66 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 13.6 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 13.62 – 14.62 kJ/gCOD <sub>rem.</sub> 12.1 – 13.7 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 12.8 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 15.68 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 12.4 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 13.9 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup> 17.8 kJ/gCOD <sub>rem.</sub> <sup>(E)</sup>	Cooney <i>et al.</i> , 1968 Andrews and Kambhu, 1969 McCarty, 1972 Zanoni and Mueller, 1982 Jewell, 1982 Heinritz <i>et al.</i> , 1990 Messenger <i>et al.</i> , 1992 Pitt <i>et al.</i> , 1995 Riley and Forster, 2002 Shizas and Bagley, 2004 Gomez <i>et al.</i> , 2007 Heidrich <i>et al.</i> , 2011
2 C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (aq.)+3O <sub>2</sub> (g) →3H <sub>2</sub> O(l) +3CO <sub>2</sub> (g)+Biomass	-893.1 kJ/mol <sub>SSU rem.</sub>	-890.0 kJ/mol <sub>SSU rem.</sub> <sup>(T)</sup>	Gallert <i>et al.</i> , 2005
3 NH <sub>4</sub> <sup>+</sup> (aq.)+1.5 O <sub>2</sub> (g) → 2H <sup>+</sup> (aq.) + NO <sub>2</sub> <sup>-</sup> (aq.)+H <sub>2</sub> O (l)	-258.0 kJ/mol <sub>N rem.</sub>	-259.0 kJ/mol <sub>N rem.</sub> <sup>(T)</sup>	Daverio <i>et al.</i> , 2003
4 NO <sub>2</sub> <sup>-</sup> (aq.)+0.5 O <sub>2</sub> (g) → NO <sub>3</sub> <sup>-</sup> (aq.)	-102.0 kJ/mol <sub>N rem.</sub>	-99.4 kJ/mol <sub>N rem.</sub> <sup>(T)</sup>	Daverio <i>et al.</i> , 2003
5 NH <sub>4</sub> <sup>+</sup> (aq.)+NO <sub>2</sub> <sup>-</sup> (aq.) → N <sub>2</sub> (g)+ 2H <sub>2</sub> O (l)	-334.6 kJ/mol <sub>N rem.</sub>	-333.0 kJ/mol <sub>N rem.</sub> <sup>(T)</sup>	Buttiglieri <i>et al.</i> , 2010
6 C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (aq.)→ 2.85CH <sub>4</sub> (g) + 2.85CO <sub>2</sub> (g)	-132.8 kJ/mol <sub>SSU rem.</sub>	-131.0 kJ/mol <sub>SSU rem.</sub> <sup>(T)</sup>	Gallert <i>et al.</i> , 2005
7 CH <sub>3</sub> COOH(aq.)→ CH <sub>4</sub> (aq.) + CO <sub>2</sub> (aq.)	-12.4 kJ/mol <sub>SHAC rem.</sub>	-15.3 kJ/mol <sub>SHAC rem.</sub> <sup>(T)</sup>	Oh <i>et al.</i> , 2007
8 CH <sub>3</sub> COOH(aq.)→ CH <sub>4</sub> (g) + CO <sub>2</sub> (aq.)	-4.8 kJ/mol <sub>SHAC rem.</sub>	$\Delta h_r^\circ < 0$ <sup>(T)</sup>	Oh <i>et al.</i> , 2007
9 CH <sub>3</sub> COOH(aq.)→ CH <sub>4</sub> (g) + CO <sub>2</sub> (g)	15.2 kJ/mol <sub>SHAC rem.</sub>	$\Delta h_r^\circ > 0$ <sup>(T)</sup>	Oh <i>et al.</i> , 2007
10 HAC digestion (aq.) (methanogenesis)	-9.8 kJ/mol <sub>SHAC rem.</sub>	$\Delta h_r^\circ < 0$ <sup>(T)</sup>	Oh <i>et al.</i> , 2010
11 HPRO digestion (aq.) (acetogenesis & methanogenesis)	0.6 kJ/mol <sub>SHPRO rem.</sub>	$\Delta h_r^\circ > 0$ $\Delta h_{r,11}^\circ > \Delta h_{r,10}^\circ$ <sup>(T)</sup>	Oh <i>et al.</i> , 2010
12 HBU digestion (aq.) (acetogenesis & methanogenesis)	6.8 kJ/mol <sub>SHBU rem.</sub>	$\Delta h_r^\circ > 0$ $\Delta h_{r,12}^\circ > \Delta h_{r,11}^\circ$ <sup>(T)</sup>	Oh <i>et al.</i> , 2010
13 HVA digestion (aq.) (acetogenesis & methanogenesis)	16.9 kJ/mol <sub>SHVA rem.</sub>	$\Delta h_r^\circ > 0$ <sup>(T)</sup> $\Delta h_{r,13}^\circ > \Delta h_{r,12}^\circ$ <sup>(T)</sup>	Oh <i>et al.</i> , 2010

Theoretical <sup>(T)</sup> and Experimental Data <sup>(E)</sup>

**Table 5** – Specific heat yields (or energy content) estimated for the different substrates used in the model

	$S_{SU}$	$S_{AA}$	$S_{FA}$	$S_{HVA}$	$S_{HBU}$	$S_{HPRO}$	$S_{HAC}$
<b>Oxidation heats (kJ/gCOD<sub>rem.</sub>)</b>	-15.23	-14.38	-14.64	-14.11	-14.13	-14.16	-14.28
<b>Oxidation + CO<sub>2</sub> stripping heats (kJ/gCOD<sub>rem.</sub>)</b>	-14.62	-13.80	-13.62	-13.64	-13.65	-13.64	-13.67

**Table 6** – Evolution of the organic loading rate (OLR) applied to the ATAD reactor

Time (d)	0.2	1.2	2.2	3.2	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0	13.0
OLR (Kg COD/m <sup>3</sup> d)	2.95	3.00	3.03	3.35	3.81	3.51	3.53	4.05	0.00	4.90	5.56	5.24	5.57	4.42

**Table 7** – Characterization of the influent

	Fraction of lipids	Fraction of proteins	Fraction of carbohydrates	Fraction of inert
Baseline Characterisation	19%	25%	19%	37%
Characterisation 1	15%	20%	28%	37%
Characterisation 2	22%	31%	10%	37%

**Figure 1** - Schematic representation of the matrix restructuration

**Figure 2** - Schematic representation of the mass balance in an aerated biological closed reactor

**Figure 3** - Schematic representation of the enthalpy balance in a C-CSTR

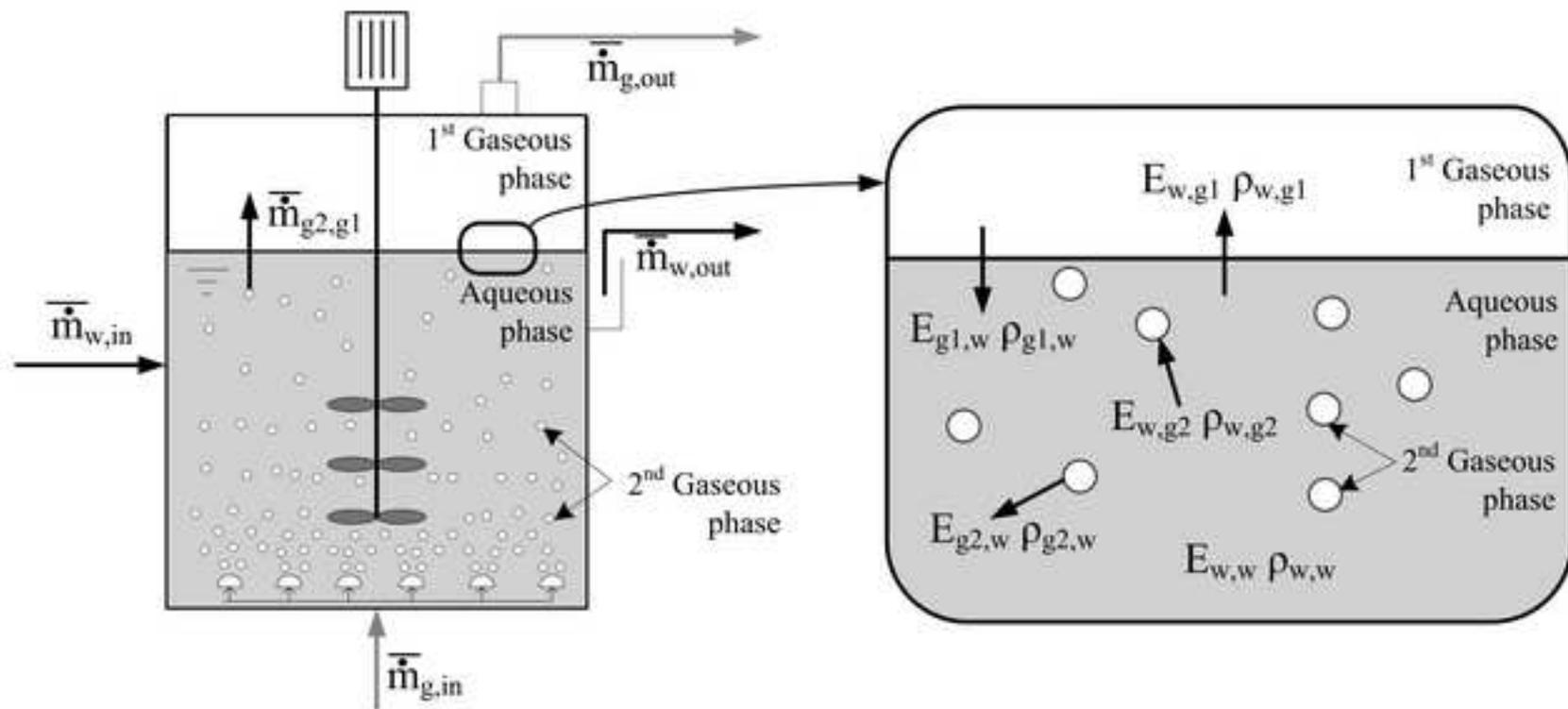
**Figure 4** – (a) Total enthalpy produced and consumed in the system with the contribution of each thermal flux, (b) Transformation heat fluxes

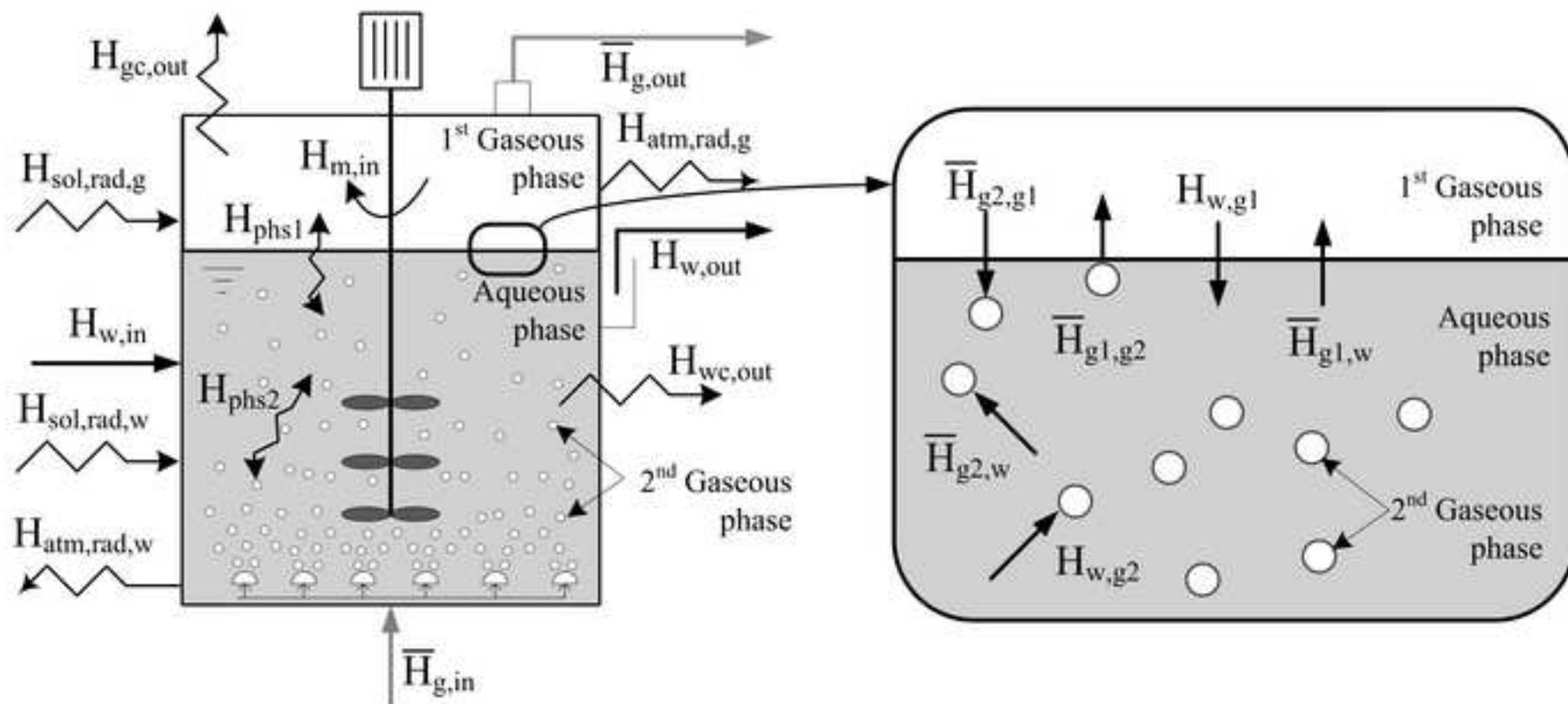
**Figure 5** – (a) Experimental and simulation results for the full scale ATAD, (b) Total enthalpy produced and consumed in the system with the contribution of each thermal flux

**Figure 6** – Behaviour of the temperature in a full scale ATAD for constant OLR and variable aeration flows

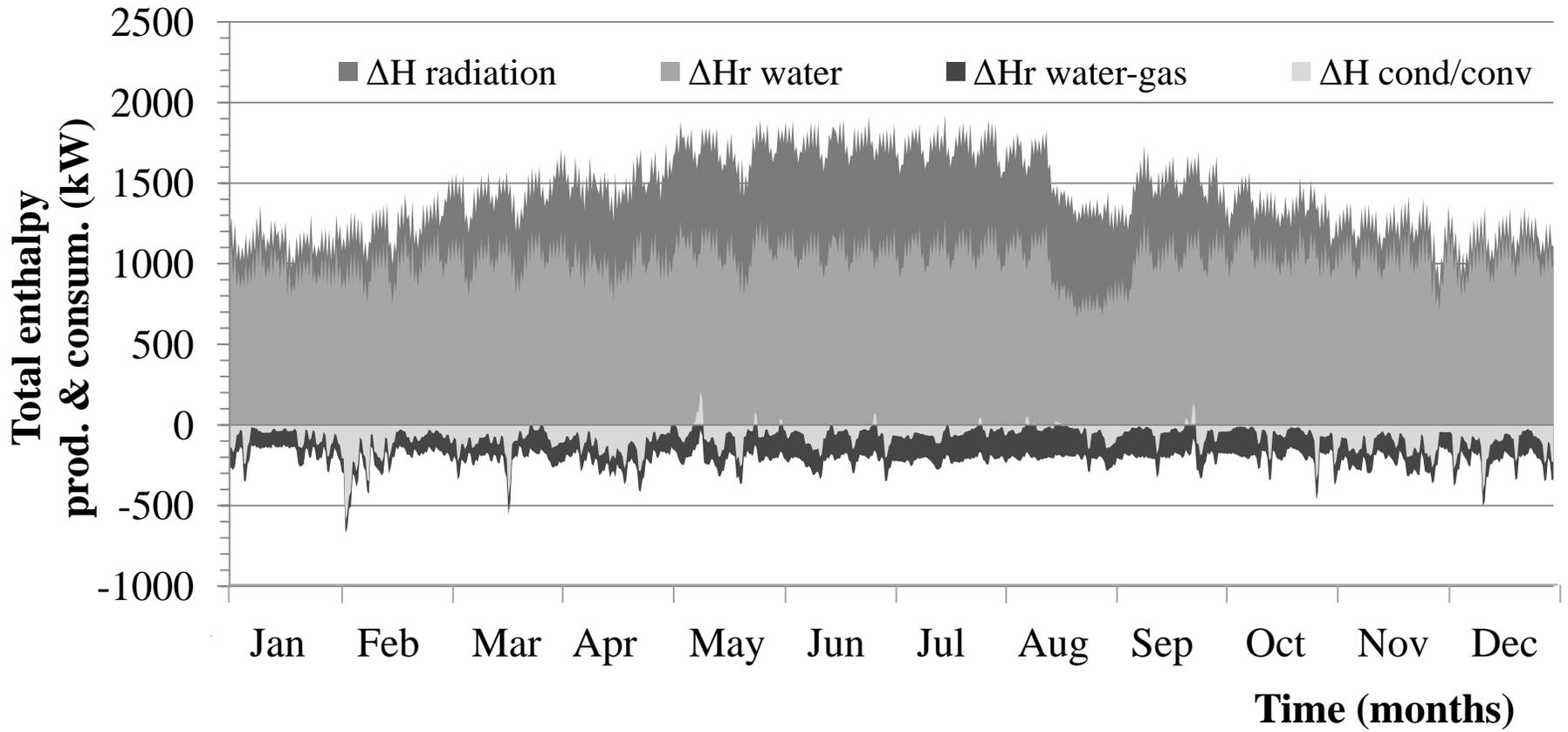
**Figure 7** – (a) Temperature evolution for different influent characterizations (b) Aqueous transformation heats (specific heat yield) for different influent characterizations

	AQUEOUS $\bar{M}_w (NC_w \times 1)$	GASEOUS $\bar{M}_g (NC_g \times 1)$	SOLID $\bar{M}_s (NC_s \times 1)$	
$\bar{p}_{w,w}$	$\tilde{E}_{w,w} (NT_w \times NC_w)$			<b>Transformations in the aqueous phase</b>
$\bar{p}_{g,g}$		$\tilde{E}_{g,g} (NT_g \times NC_g)$		<b>Transformations in the gas phase</b>
$\bar{p}_{w,g} = \bar{p}_{g,w}$	$\tilde{E}_{w,g} (NT_{wg} \times NC_w)$	$\tilde{E}_{g,w} (NT_{wg} \times NC_g)$		<b>Liquid-Gas / Gas-Liquid transfers:</b> Evaporation / Condensation & Stripping / Absorption
$\bar{p}_{w,s} = \bar{p}_{s,w}$	$\tilde{E}_{w,s} (NT_{ws} \times NC_w)$		$\tilde{E}_{s,w} (NT_{ws} \times NC_s)$	<b>Liquid-Solid / Solid-Liquid transfers:</b> Precipitation / Dissolution
$\bar{p}_{g,s} = \bar{p}_{s,g}$		$\tilde{E}_{g,s} (NT_{gs} \times NC_g)$	$\tilde{E}_{s,g} (NT_{gs} \times NC_s)$	<b>Gas-Solid / Solid-Gas transfers:</b> Deposition / Sublimation
	...	...	...	

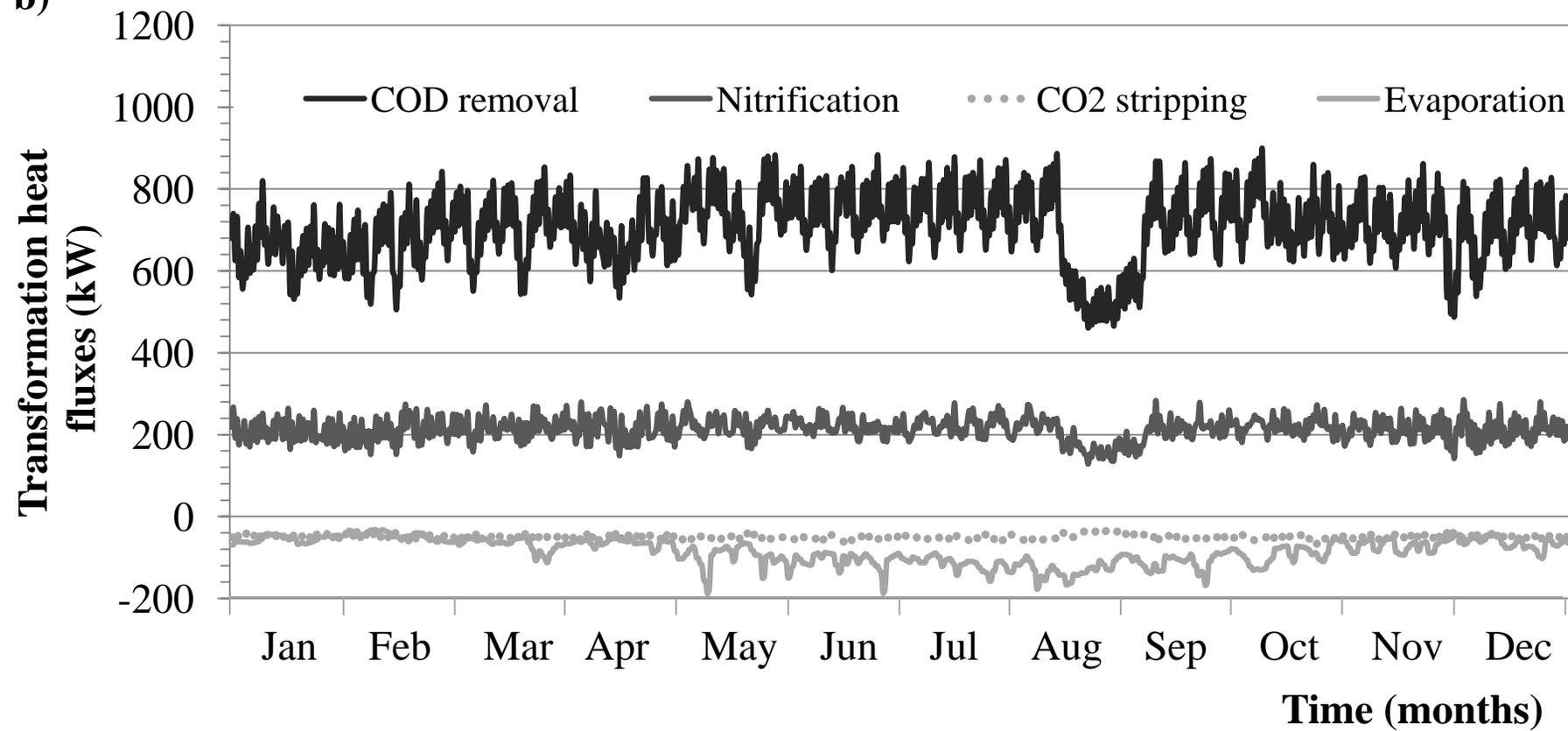




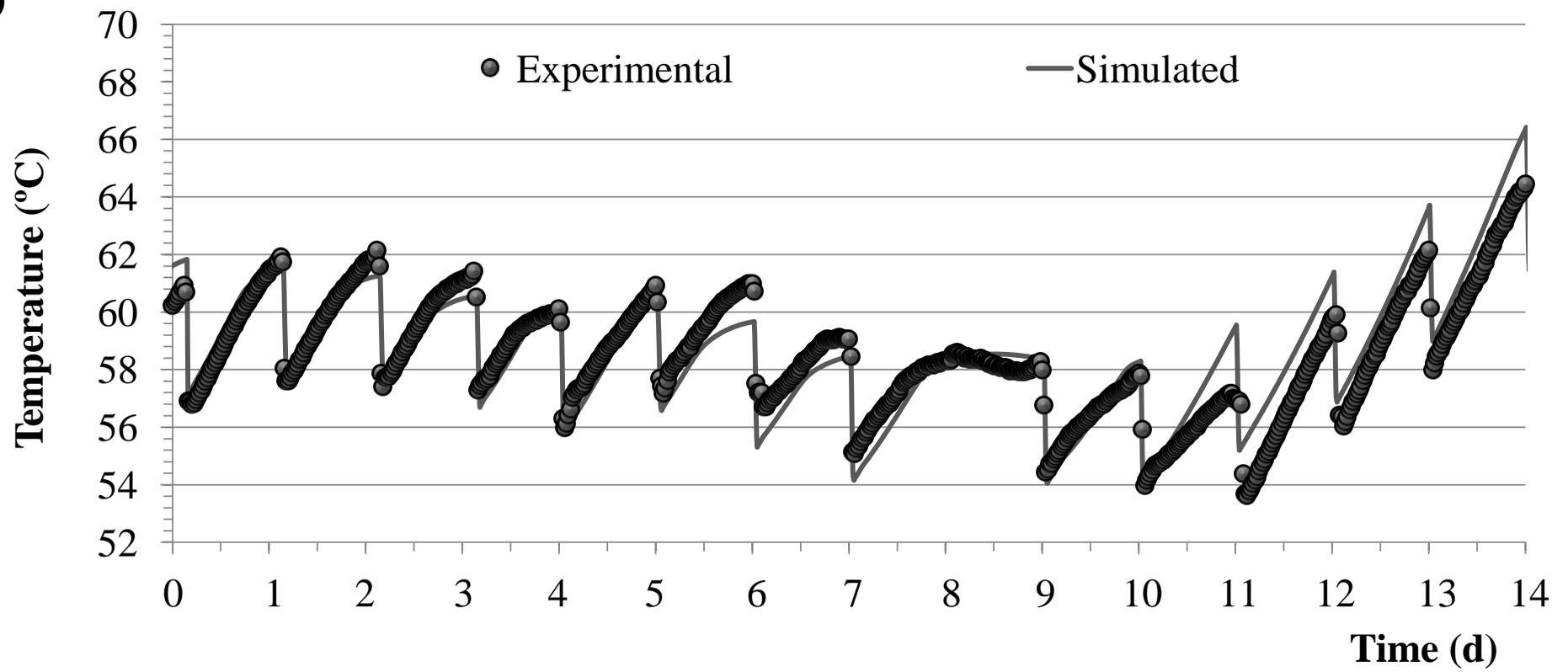
a)



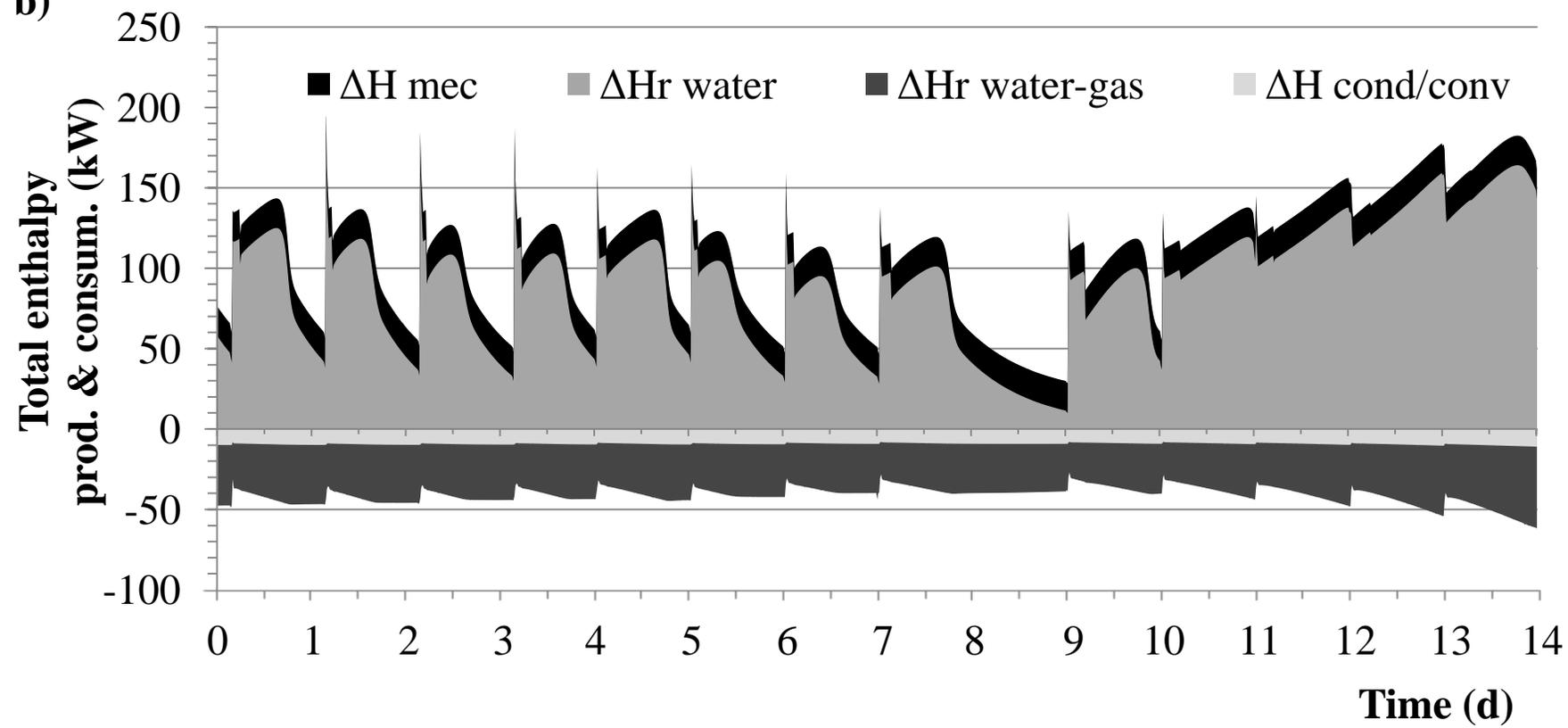
b)

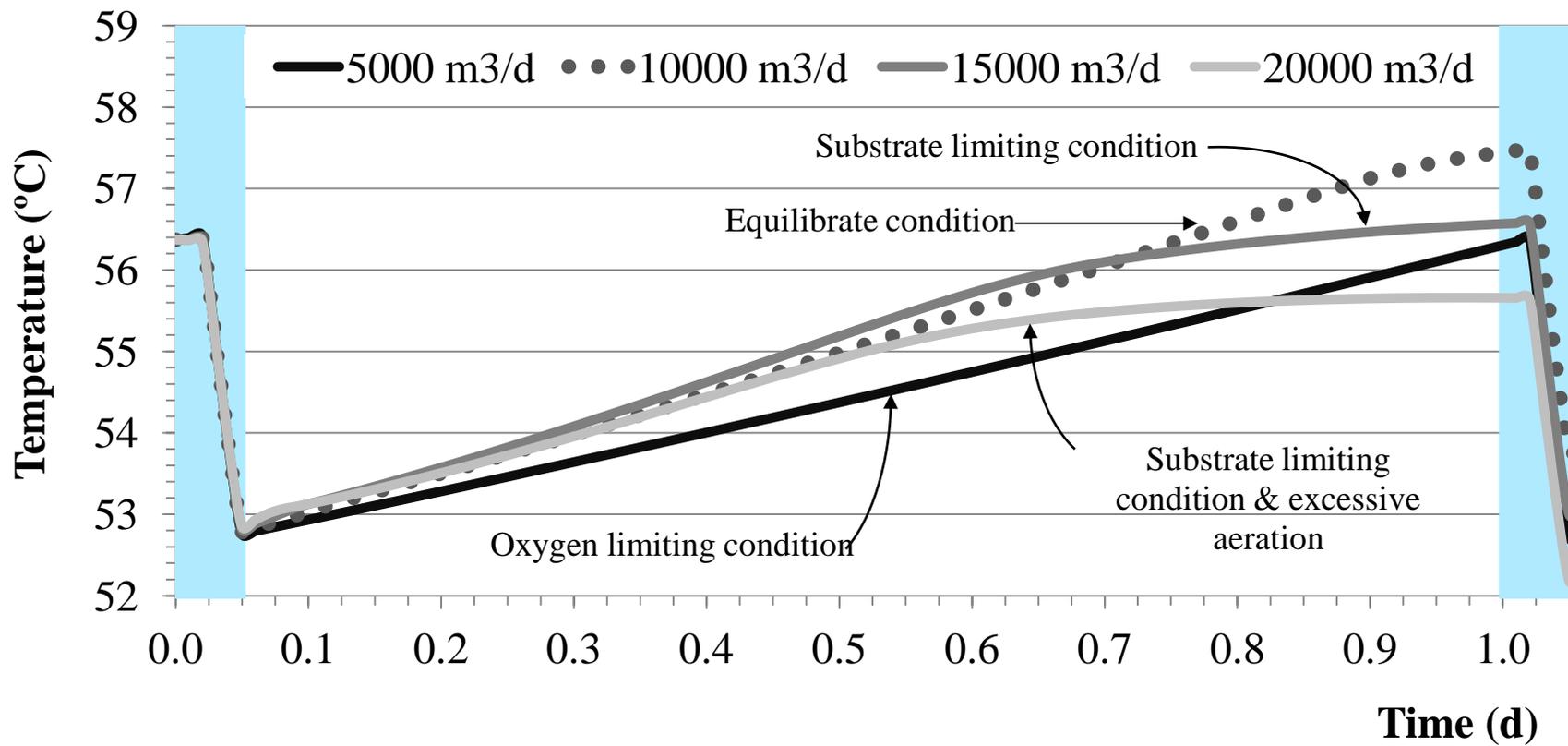


a)

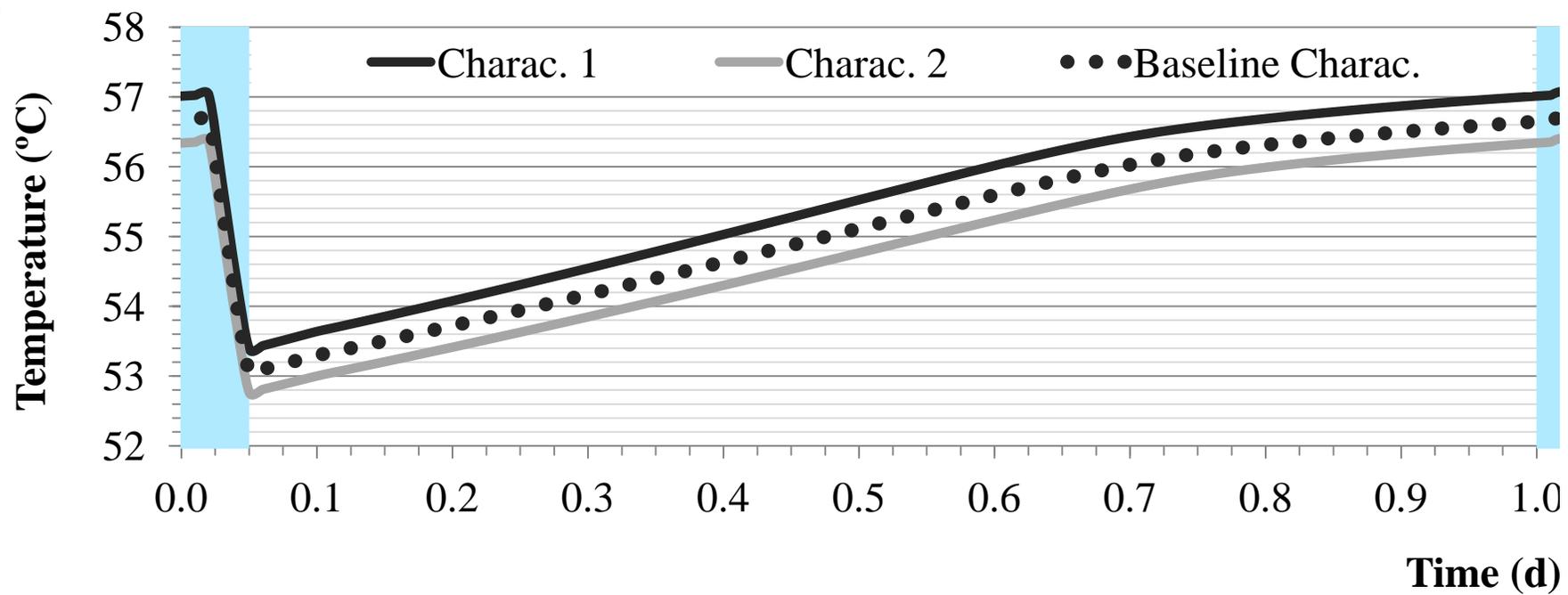


b)

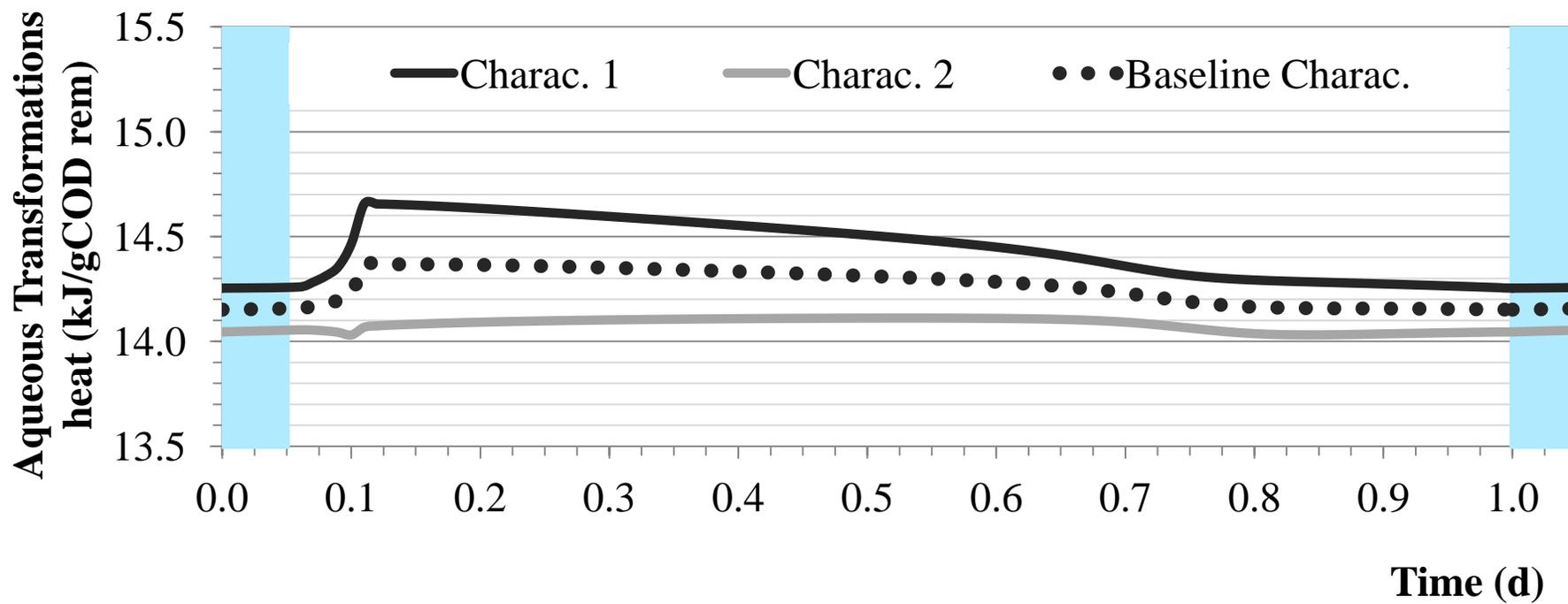




a)



b)



- New methodology for dynamic  $\Delta H_r$  prediction in biological reactors using Hess's law
- Methodology implemented in a plant-wide modelling methodology
- Simultaneous calculation of the conventional mass balances and the enthalpy balance
- Multi-phase matrix structure to facilitate the prediction of mass and heat fluxes
- Methodology easily integrated into the numerical solution of existing models