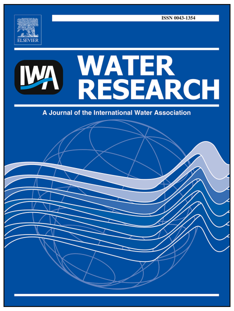

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EXTENDED PLANT-WIDE MODELLING METHODOLOGY

E-PWM

CALORIFIC ENERGY CONTINUITY

MASS & CHARGE CONTINUITY (PWM)

MULTI-PHASE REACTORS

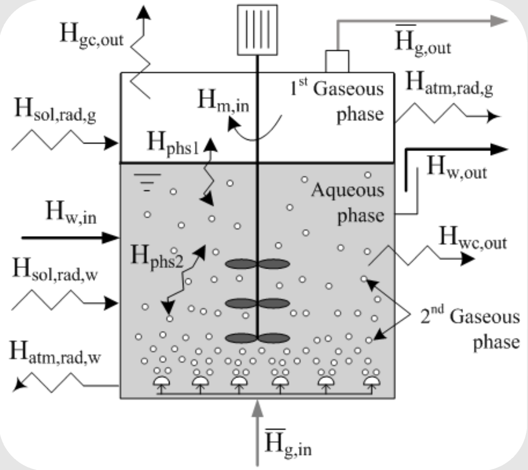
HESS S LAW

$$\Delta H^{\circ}_{r} = \sum \nu_{\text{products}}\ \rho\ \Delta h^{\circ}_{f\,(\text{products})} - \sum \nu_{\text{reactants}}\ \rho\ \Delta h^{\circ}_{f\,(\text{reactants})}$$

GUJER MATRIX NOTATION

$$\Delta H^{\circ}_{r} = \left(\overline{\Delta h_{f}{}^{\circ}}\right)^{T} \tilde{E}^{T}\ \bar{\rho}$$

ENTHALPY BALANCE



Methodology easily integrated into the numerical solution of any existing mathematical model

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

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Abstract

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

Keywords

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

NOMENCLATURE

$A_{bubbles}$	Contact area between aqueous phase and 2nd gas phase (m^2)
A_g	1st gas phase surrounding area (m^2)
A_{tank}	Contact area between aqueous phase and 1st gas phase (m^2)
A_w	Aqueous phase surrounding area (m^2)
$\overline{Cp_i}$	Specific heat capacity of i gaseous phase components at constant pressure (kJ gE^{-1} K^{-1})
$Cp_{w,H2O}$	Specific heat capacity of water at constant pressure (kJ $gH2O^{-1}$ K^{-1})
$\widetilde{E}_{i,j}$	i phase stoichiometric matrix for the transformations between i and j phase
g	Gravitational acceleration (m s^{-2})
Gr	Grashof number
$\bar{h}_{i,ref}$	Reference enthalpy of the i gaseous phase components (kJ gE^{-1})
$h_{w,ref,H2O}$	Reference enthalpy of water (kJ $gH2O^{-1}$)
H_{Act}	Enthalpy transmitted from the actuators (kJ d^{-1})
H_{atm_rad}	Longwave atmospheric radiation flux (kJ d^{-1})
$H_{Cond/Conv}$	Surface conduction and convection enthalpy flux (kJ d^{-1})
$\bar{H}_{in}$	Input enthalpy (kJ d^{-1})
$\bar{H}_{out}$	Output enthalpy (kJ d^{-1})
H_{sol_rad}	Shortwave solar radiation flux (kJ d^{-1})
H_T	Net heat exchange of the analysed phase (kJ d^{-1})
H_{trans}	Heat released or absorbed by the transformations in the analysed phase (kJ d^{-1})
$k_{sol,rad}$	Total energy incident on the surface (kJ d^{-1} m^{-2})
k_{wls}	Heat conduction through walls and pipes coefficient (kJ d^{-1} K^{-1} m^{-2})
$\bar{\dot{m}}_{i,in}$	Inlet i phase mass flux (gE d^{-1})
$\bar{\dot{m}}_{i,j}$	Mass flux transport between i and j phases (gE d^{-1})
$\bar{\dot{m}}_{i,out}$	Outlet i phase mass flux (gE d^{-1})
$\bar{M}_i$	Mass vector for the components present in the i phase (gE)

$n_{phs,i}$	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 (kJ d^{-1})
Pr	Prandtl number
T_{atm}	Atmospheric temperature (K)
T_i	i phase temperature (K)
$T_{i,in}$	i phase inflow temperature (K)
$\overline{T}_{i,ref}$	Temperature corresponding to the reference enthalpy of the i gaseous phase components (K)
$T_{w,ref,H2O}$	Temperature corresponding to the reference enthalpy of water (K)
$\overline{X}_i$	Mass fraction of the gaseous phase components (gE_i gE_{phase}^{-1})

Greek Symbols

$\alpha_{phs,i}$	Correction factor for surfaces facing up (aqueous and i gaseous phases conduction/convection)
α_{rad}	Solar absorptivity
β_{air}	Atmospheric radiation factor
β_{phs}	Coefficient of volume expansion (K^{-1})
δ	Characteristic length (m)
Δh_f	Specific formation enthalpy (kJ gE^{-1})
Δh_r	Specific reaction enthalpy (kJ gE^{-1})
ΔH_r	Net reaction enthalpy (kJ d^{-1})
ε_{atm}	Surface emissivity
η_m	Efficiency of engines/aeration systems
$\overline{\lambda}_i$	Thermal conductivity of the i gaseous phase components (kJ d^{-1} K^{-1} m^{-1})
λ_{atm}	Surface reflectivity
μ_{g1}	Dynamic viscosity of the gaseous phase components (kgE m^{-1} s^{-1})
$\nu_{i,j}$	Rate coefficient for component i on process j (gE_i $gE_{reference\ component}^{-1}$)
$\overline{\rho}_{i,j}$	Kinetic rate for the transformations between i and j phases ($gE_{removed\ component}$ d^{-1})
σ	Stefan Boltzman constant (kJ d^{-1} m^{-2} K^{-4})
υ_{g1}	Kinematic viscosity of the gaseous phase components (m^2 s^{-1})

Superscripts

*	Absolute temperature (ºC)
º	Standard state values (25ºC)

Subscripts

g	gaseous phase
g_1	1st gaseous phase
g_1	2nd gaseous phase
in	Input
k	No. of state variables in the water phase
m	No. of state variables in the 1st gaseous phase
n	No. of transformations in the water phase
out	Output
s	solid phase
z	No. of state variables in the 2nd gaseous phase
w	Aqueous phase

1. INTRODUCTION

Operating temperature plays an important role in wastewater treatment efficiency (Metcalf and Eddy, 2004). Temperature dynamics affect microbial activity as well as physicochemical properties, such as dissolved oxygen saturation concentration, diffusivity, viscosity, density and the settling velocity (Sedory and Stenstrom 1995). An increased temperature of a few degrees might stimulate the metabolic activity of the bacteria, while a substantial reduction of several degrees would result in reduced process stability, albeit temporarily, and a possible shift in the population of the reactor (Gallert and Winter, 2005). The causes of these temperature variations are often due to a combination of different factors. The most representative are conduction/convection phenomena, short-wave and long-wave radiations, the heat transmitted by the actuators and, to a greater or lesser degree, the heat produced or consumed by biochemical, chemical or physico-chemical transformations. The influence of each term in the system is varied and depends largely on the analysed process and climate of the place. In the activated sludge units, a typical diurnal temperature difference between water inlet and outlet fluxes only varies between 0.5 and 1 degree (Makinia *et al*, 2005). However, in some parts of the world, treatment systems are subjected to significant winter cooling and summer heating. In some nontemperate zones for instance, the atmospheric diurnal air temperature variation can be considerable, ranging from 2 degrees during the early morning to over 25 degrees during mid-afternoon (Paul, 2013), affecting considerably to the water temperature. In membrane bioreactors, the temperature rise in the tank may be quite significant comparing with the activated sludge reactors because of the higher biological heat production. These reactors have a higher biomass concentration and bacterial activity, which implies a higher biological heat production due to the exothermicity of the oxidation, nitrification and denitrification reactions (Sethi *et al.*, 2011). In sludge line processes, the effect of temperature has greater importance and practically all units work above atmospheric temperature. The anaerobic digestion for example, is often an endothermic process which operates around 35 or 55 degrees, thus requiring a heat supply to maintain the digester temperature and support the microbial activity (Inoije *et al.*, 1996), and in the Autothermal Thermophilic Aerobic Digestion (ATAD) the organic matter is oxidized under aerobic conditions with a concomitant biological heat release that is able to maintain thermophilic temperatures. Despite the clear knowledge that exists to date on the phenomena involved in the transfer of heat, the exact influence of temperature is difficult to determine because of its interaction with mass transfer, chemical equilibrium and growth rate (Van Hulle *et al.*, 2010). It is for this reason that the joint modelling of biological transformations and accurate heat transfer models are becoming increasingly practical and necessary, not only to predict the temperature of the system, but also to identify the diverse heat flows, to analyse the contribution of these in the heat transfers, to relate the temperature variations with the chemical, biochemical and physico-chemical transformations and, ultimately, to understand the process better. An accurate temperature model allows determining a precise microbial activity, which is extremely important aspect in the analysis of new operational strategies as well as new configurations (www.novedar.com). Nowadays, thermal processes are increasingly being incorporated into treatment plants (Daigger, 2011), making temperature prediction models essential for a proper use and recovery of the heat.

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

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

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

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

Plant-Wide Modelling (PWM) methodology (Grau *et al.*, 2007) was proposed for the systematic construction of compatible unit-process models for describing the dynamic behaviour of the water and sludge lines in an integrated way. This methodology is based on selecting the set of process transformations required to model all unit-process elements incorporated into each specific WWTP. For the unification and standardisation of this set of biochemical, chemical and physico-chemical transformations, the incorporation of activation/inhibition terms in the kinetics must be accurate, in order to reproduce the appropriate bacterial activity under aerobic, anoxic and anaerobic conditions. Additionally, this unification permits the definition of a unique component vector for the whole plant, without the need to develop specific transformers to interface the unit-process models, making it a flexible methodology for both the definition of new reactions or processes and defining new units. The accurate definition of the stoichiometry ensures the elemental mass (in terms of C, N, O, H, P or other additional elements) and charge continuity in all the transformations. In order to achieve this, some components must act as source-sink terms (or mass “compensation terms”) for the correct adjustment of the C, N, O, H, P and charge balances (Reichert *et al*., 2001; de Gracia *et al*., 2006). More details of this methodology can be found in Grau *et al.* (2007).

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

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

The description of ASM models (Henze *et al.*, 2000) is based on the Gujer matrix notation that presents the process kinetics and stoichiometry in a single product of matrices ($\tilde{E}\cdot\bar{\rho}$). These models only considered the water phase reactions, but in current technologies different aqueous, gaseous or solid phases can be considered in a single unit-process multiplying the equations required to models definition. With the purpose to develop flexible and easily understood models, the E-PWM methodology proposes a general procedure for multi-phase model construction in which mass balances are constructed systematically considering as many type of phases (gas, liquid, solid) and number (1 liquid + 1 gas, 1 liquid + 2 gas phases, etc.) as required in each case study. The first step of the procedure consists on the selection of the phases and transformations to model the WWTP under study. Each phase (aqueous, gaseous or solid) as an independent system with its corresponding mass vector (M) will be considered. Accordingly, each phase will have an independent matrix ($\tilde{\overline{E}}\cdot\bar{\rho}$) to define the transformations that take place in the phase (such as, for example, bacterial growth, or chemical equilibria reactions in the aqueous phase) and another set of matrices ($\tilde{\overline{E}}\cdot\bar{\rho}$) to define the transformations between different phases (such as evaporation/condensation, stripping/absorption, precipitation/dissolution or deposition/sublimation). Thus, the model will be constructed using as many matrices as phases and interactions between phases. This modular construction can be visualized by means of the generic example depicted in Figure 1. And the second step consists on the definition of the mass balances of the unit processes. The definition of the set of matrices allows a systematic mass balance description based on the structure shown in equation 1.

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

i = 1, 2 … No. phases (number of phases)
j = 1, 2… No. adj. phase (number of adjacent phases to phase i)

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

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

2.2. New methodology for temperature prediction based on formation enthalpies

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

$$\Delta h^{\circ}_{r} = \sum \nu_{\text{products}} \, \Delta h^{\circ}_{f\,(\text{products})} - \sum \nu_{\text{reactants}} \, \Delta h^{\circ}_{f\,(\text{reactants})} \tag{2}$$

To calculate the net enthalpy change of reaction (ΔH^{o}_{r} in KJ d^{-1}) instead, multiplying this specific enthalpy change of reaction by its corresponding kinetic and stoichiometry is sufficient:

$$\Delta H^{\circ}_{r} = \sum \nu_{\text{products}} \, \rho \, \Delta h^{\circ}_{f\,(\text{products})} - \sum \nu_{\text{reactants}} \, \rho \, \Delta h^{\circ}_{f\,(\text{reactants})} \tag{3}$$

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

$$\dot{x} = \tilde{\bar{E}}^{T} \, \bar{\rho} \tag{4}$$

$$\Delta H^{\circ}_{r} = \left(\overline{\Delta h_{f}}^{\circ}\right)^{T} \dot{x} \tag{5}$$

where,

$$\overline{\Delta h}_f^\circ = \begin{pmatrix}\Delta h_{f\,1}\\ \Delta h_{f\,2}\\ \vdots\\ \Delta h_{f\,j}\\ \vdots\\ \Delta h_{f\,k}\end{pmatrix}; \qquad \widetilde{E} = \begin{pmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1j} & \cdots & \nu_{1k}\\ \nu_{21} & \nu_{22} & \cdots & \nu_{2j} & \cdots & \nu_{2k}\\ \vdots & \vdots & & \vdots & & \vdots\\ \nu_{i1} & \nu_{i2} & \cdots & \nu_{ij} & \cdots & \nu_{ik}\\ \vdots & \vdots & & \vdots & & \vdots\\ \nu_{n1} & \nu_{n2} & \cdots & \nu_{nj} & \cdots & \nu_{nk}\end{pmatrix}; \qquad \overline{\rho} = \begin{pmatrix}\rho_1\\ \rho_2\\ \vdots\\ \rho_i\\ \vdots\\ \rho_n\end{pmatrix};$$

This close relationship maintaining mass and heat balances makes it a systematic methodology that can be easily integrated into the numerical solution of any existing mathematical model. The only requisite is the definition of the enthalpies of formation of the compounds present in these transformations. For this paper a set of transformations have been selected from the E-PWM library which gather all the components and transformations able to describe aerobic, anoxic and anaerobic COD biodegradation; nitrogen removal in two steps ($NO_3^- \rightarrow NO_2^- \rightarrow N_2$); anaerobic ammonia oxidation (Anammox process); aerobic or anaerobic sludge digestion; as well as, sludge pretreatments. Enthalpies of formation needed for the definition of these transformations are summarized in Table 1 and Table 2.

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

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

One illustrative example of the usefulness of the presented E-PWM methodology can be shown in aerated biological closed reactors. In these, an aqueous phase coexists with two gaseous phases; one corresponds to the total volume occupied by the bubbles submerged in the mixed liquor (gas hold-up) and the other one to the volume of the gas in contact with the free surface of the mixed liquor (off-gas). The distinction of these volumes represents an interesting advantage over other simpler models, both for the oxygen transfer estimation, as for the correct prediction of the temperature in each phase.

3.1. Mass balance for an aerated biological closed reactor

For the analysis of three phases, three mass balances are necessary, as shown in equations 6, 7, and 8.

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

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

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

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

3.2. Heat balance for an aerated biological closed reactor

The completely mixing assumption commonly used in wastewater treatment plant process modelling, permits thermal uniformity in the reactor, avoiding temperature gradients. Thus, based on the energy conservation principle, the general one-dimensional dynamic heat transfer model includes biochemical, chemical or physico-chemical heat transfers (H_{trans}), conduction and convection fluxes ($H_{Cond/Conv.}$), heat energy fluxes transmitted by the actuators ($H_{Act.}$) and short-wave (solar) and long-wave (atmospheric) radiations ($H_{sol\_rad.}$, $H_{atm\_rad.}$), as can be shown in equation 9.

$$\left(\frac{d\,H_T}{dt}\right)_{phase} = \sum H_{trans} + \sum H_{Cond/Conv} + \sum H_{Act} + \sum H_{sol\_rad} + \sum H_{atm\_rad} + \sum \overline{H}_{in} + \sum \overline{H}_{out} \tag{9}$$

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

$$\begin{aligned}\left(\frac{d\,H_w}{dt}\right) = &-\left(\overline{\Delta h}_{f\,w}\right)^T\left(\tilde{E}^T_{w,w}\,\bar{\rho}_{w,w}\right) - \left(\overline{\Delta h}_{f\,w}\right)^T\left(\tilde{E}^T_{w,g1}\,\bar{\rho}_{w,g1}\right) - \left(\overline{\Delta h}_{f\,g1}\right)^T\left(\tilde{E}^T_{g1,w}\,\bar{\rho}_{g1,w}\right)\\ &-\left(\overline{\Delta h}_{f\,w}\right)^T\left(\tilde{E}^T_{w,g2}\,\bar{\rho}_{w,g2}\right) - \left(\overline{\Delta h}_{f\,g2}\right)^T\left(\tilde{E}^T_{g2,w}\,\bar{\rho}_{g2,w}\right) + H_{w,g1} + H_{w,g2} + H_{w,in} - H_{w,out}\\ &- H_{phs1} - H_{phs2} - H_{wc,out} + H_{m,in} - H_{atm,rad,w} + H_{sol,rad,w}\end{aligned} \tag{10}$$

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

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

These expressions in Figure 3 have been schematically represented and the definition of each term in Table 3. Thus, the first term of the water heat balance $\left(\left(\overline{\Delta h}_{f\,w}\right)^T\left(\tilde{E}^T_{w,w}\,\bar{\rho}_{w,w}\right)\right)$ refers to the heat associated to the transformations that take place in the aqueous phase, namely, it encompasses the heat of all transformations that occur in this phase. The second term $\left(\left(\overline{\Delta h}_{f\,w}\right)^T\left(\tilde{E}^T_{w,g1}\,\bar{\rho}_{w,g1}\right)\right)$ provides the stoichiometric enthalpies of formation of the components present in the aqueous phase, and the third term $\left(\left(\overline{\Delta h}_{f\,g1}\right)^T\left(\tilde{E}^T_{g1,w}\,\bar{\rho}_{g1,w}\right)\right)$ the stoichiometric enthalpies of formation of the components present in the first gaseous phase. Applying the first law of thermodynamics, the sum of both terms refers to the water-gas/gas-water convective transferences, namely, the heat transferred due to the stripping/absorption and evaporation/condensation transferences. In such a transfer, besides heat production or consumption, an enthalpy associated to the matter is transferred between the phases, producing an increase in the net heat of the target phase, though not of the specific heat. In the model these terms have been defined as enthalpy inputs and outputs due to transformations, as can be seen in Table 3.

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

4. VALIDATION OF THE METHODOLOGY FOR ESTIMATING TRANSFORMATION HEAT (ΔH_r^o)

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

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

Despite numerous experimental studies published, there is no consensus on the determination of the specific heat yields (see Table 4), although it has been estimated an approximate range of 12–18 kJ $gCOD^{-1}$ removed. These discrepancies can be attributed to the heterogeneity in the samples' composition due to the diversity in the organic components present (Cooney *et al.*, 1968). It is also important to note that, although the enthalpy change of reaction values proposed in literature are attributed to the oxidation of organic materials, these experimental estimations implicitly include other smaller transformation heats like, for example, those associated with hydrolysis or CO_2 stripping. In order to show the additional information offered by the proposed E-PWM methodology, Table 5 first row presents the theoretical specific heat yields for the seven carbonaceous substrates included in the model under study, showing the small differences associated with substrate composition, but within the range proposed in literature. Additionally, the second row illustrates the expected changes in the theoretical heats when substrate oxidation and CO_2 stripping transformations are both considered in the calculations, demonstrating the relevance of taking into account all the simultaneous transformations. This fact can explain some of the discrepancies found in the experimental results presented in the literature.

Once the appropriate calculation of the specific heat yields has been validated, the applicability of the proposed E-PWM methodology for the dynamic simulation of heat fluxes and temperature prediction has been analysed. For this, two illustrative examples have been constructed and implemented in the WEST simulation platform (www.mikebydhi.com), for its subsequent analysis.

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

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

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

Figure 4b shows a detailed description of the main heat fluxes within the reactors, differentiating between the heat supplied by the biological transformations and the heat consumed by evaporation and stripping. Simulations results clearly show how the most significant heat fluxes are due to COD removal (denitrification in anoxic reactors and heterotrophic growth in aerobic reactors) and nitrification reactions. To a lesser extent, but also relevant is the stripping of CO_2 and evaporation.

Simulation results (not presented) have shown that the expected overall increase in the water temperature from influent to effluent ranges between 0.8 and 1.5 degrees depending on the radiation term, coinciding with the ranges previously published by la Cour Jansen *et al.* (1992) and Makinia *et al* (2005). The proposed E-PWM methodology facilitates a detailed description of the contribution of different transformations in the heat flows and temperature variations. For example, at this particular case-study, simulation results show that the nitrification and heterotrophic growth reactions increase the tank temperature 0.6-0.8 degrees while denitrification only by 0.23 degrees. Evaporation and stripping reactions are widely influenced by atmospheric temperature, and decrease the temperature by 0.05-0.2 degrees. As expected, the effect of transformation heats in process temperature is not very relevant in conventional activated sludge reactors. However, it can be very significant in other processes that exhibit higher biological activity and lower heat transport with the environment like, for example, the Autothermal Thermophilic Aerobic Digesters (ATAD).

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

The ATAD digesters exhibit a high organic matter oxidation, being able to maintain thermophilic conditions without the external addition of heat (except recirculations/mixing energy). To analyse the predictive capacity of the methodology applied to an ATAD reactor, the first step has been the comparison between the simulation results and the experimental data obtained in the full scale ATAD at the Tudela WWTP (de Garcia *et al.*, 2009; Gomez *et al.*, 2007). This ATAD digester is a completely stirred tank reactor with a total effective volume of 350 m^3. In the analysed 14-day period, the digester operated at 10 days hydraulic retention time with discontinuous charges and discharges of the reactor every 24h. A period with abrupt changes in the organic loading rate (OLR) was selected for the validation of the thermal model under both oxygen limiting and substrate limiting conditions. To achieve these two conditions, the aeration flow rate of 9,200 m^3 d^{-1} remained constant, gradually increasing the OLR (see Table 6). A detailed description of the stoichiometric, kinetic and physico-chemical parameters can be found in de Gracia *et al.* (2009).

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

By analysing the thermal flux of the system (Figure 5b), it can be seen that biological processes (ΔHr water) are the most important heat flux contributors, representing 60-70% of the heat in the process. The contour of this flux area shows the evolution of organic matter oxidation, clearly differentiating substrate limiting and oxygen limiting areas. The heat dissipated due to the liquid and gas phase transformations (ΔHr water-gas) is the second most important heat flux, representing 15-30% of the heat in the process. Of this percentage, 10% corresponds to CO_2 stripping, and the remaining 90% to the heat lost by evaporation. In this example, atmospheric and solar radiation have not been graphed since they were negligible compared to other terms.

The proposed E-PWM methodology also makes possible a detailed dynamic analysis of the different terms in heat generation and transport as a function of the influent load or operational strategies. Next examples briefly show the effect of ventilation and the substrate fed in the ATAD temperature.

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

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

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

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

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

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

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

5. CONCLUSIONS

The paper presents a new methodology, based on the well-known Hess’s law, for the rigorous and systematic calculation of heat balances in biochemical reactors. Starting from a complete description of model components stoichiometry and enthalpies of formation, the proposed modelling methodology, called Extended Plant-Wide Modelling (E-PWM), has integrated successfully the simultaneous calculation of both the conventional mass balances and the heat balances in an expandable multi-phase matrix structure, which facilitates a detailed prediction of the main heat fluxes in the biochemical reactors. Without wanting to focus on the mere calculation of heat exchanges in a single reactor, the heat balance has been also integrated into the CEIT Plant-Wide Modelling methodology (Grau *et al*, 2007) in order to conduct a comprehensive analysis of entire WWTPs.

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

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References

Adriaanse, N., Dekker, H., Coops, J., 1965. Heats of combustion of normal saturated fatty acids and their methyl esters, Rec. Trav. Chim. Pays/Bas, 84, 393-407.

Andrews J.F., Kambhu K., 1969. Aerobic thermophilic process for the biological treatment of wastes – simulation studies. J Water Pollut. Control Fed. 41. 127-141.

Argaman, Y., Adams, C.E. Jr., 1977. Comprehensive temperature model for aerated biological systems. Prog. Water Technol. 9(2), 397–409.

Brown, R.C., 2011. Thermochemical processing of Biomass: Conversion into fuels, chemicals and power. Wiley, United Kingdom.

Brown, T.L., LeMay, H.E. Jr, Bursten, B.E., 1993. Química. La ciencia central. McGraw-Hill, Ed.5, USA.

Buttiglieri, G., Bouju, H., Malpei, F., Ficara, E., Canziani, R., 2010. Microcalorimetry: A tool to investigate aerobic, anoxic and anaerobic autotrophic and heterotrophic biodegradation. Biochemical Engineering Journal, 52(1), 25-32.

Chang R., 1999. Química, Ed 6, McGraw-Hill, México.

Constantinou, L., Gani, R., 1994. New Group Contribution Method for Estimating Properties of Pure Compounds, *AIChE J.*, 40(10), 1697-1710.

Cooney, C.L., Wang, D.I.C., Mateles, R.I., 1968. Measurement of Heat Evolution and Correlation with Oxygen Consumption during Microbial Growth. Biotech. & Bioengineering, XI, 269-281.

Copp, J.B., Jeppsson, U., Rosen, C., 2003. Towards an ASM1-ADM1 State Variable Interface for Plant-Wide Wastewater Treatment Modeling. In: Proceedings of the WEFTEC, Los Angeles Convention Center, Los Angeles, CA, USA, October 11-15.

Daigger, G.T., 2011. A practitioner’s perspective on the uses and future developments for wastewater treatment modelling. Water Science & Technology 63 (3), 516.

Daverio, E., Aulenta, F., Ligthart, J., Bassani, C., Rozzi, A., 2003. Application of calorimetric measurements for biokinetic characterisation of nitrifying population in activated sludge. Water Research, 37(11), 2723-2731.

de Gracia, M., Grau, P., Huete, E., Gómez, J., García-Heras, J.L., Ayesa, E., 2009. New generic mathematical model for WWTP sludge digesters operating under aerobic and anaerobic conditions: Model building and experimental verification. *Water Research*, 43(18), 4626-4642.

de Gracia M., Sancho L., García-Heras J.L., Vanrolleghem P.A., Ayesa E., 2006. Mass and Charge Conservation Check in Dynamic Models: Application to the New ADM1 Model. *Water Science & Technology*, **53**(1), 225-240.

Everett, D.H., Wynne-Jones, F.K., 1939. The thermodynamics of acid-base equilibria. Transaction of the Faraday Society. 35, 1380-1401

Freedman, B., Bagby, M.O., Khoury, H., 1989. Correlation of heats of combustion with empirical formulas for fatty alcohols, J. Am. Oil Chem. Soc., 66, 595-596.

Gallert, C., Winter, J., 2005. Bacterial Metabolism in Wastewater Treatment Systems. In: Jördening, H.J., Winter, J. (Eds.), Environmental Biotechnology – Concepts and Applications. Wiley-VCH, Weinheim. 1-48.

Gómez, J., de Gracia, M., Ayesa, E., de las Heras, J.L., 2007. Mathematical modelling of autothermal thermophilic aerobic digesters. *Water Research*, 41, 959-968.

Grau, P., de Gracia, M., Vanrolleghem, P., Ayesa, E., 2007. A new Plant-Wide modelling methodology for WWTPs. Water Research, 41(19), 4357-4372.

Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D.A., Rand, M.H., 2003. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier Science, Amsterdam.

Gillot, S., Vanrolleghem, P.A., 2003. Equilibrium temperature in aerated basins-comparison of two prediction models. Water Research 37, 3742-3748.

Heidrich, E.S., Curtis, T.P., Dolfing, J., 2011. Determination of the Internal Chemical Energy of Wastewater. Environ. Sci. Technology. 45, 827-832.

Heijnen, J.J., 1999. Bioenergetics of Microbial Growth. In: Flickinger, M.C. & Drew, S.W. (eds) Encyclopedia of Bioprocess Technology: Fermentation, Biocatalysis, and Bioseparation. Wiley-Interscience, New York, pp. 267–291.

Heinritz B., Gehrhardt M., Baumann F., Rogge G., Hedlich R., Ringpfeil M., 1990. Biomass production by thermophilic microorganisms simultaneously using reaction heat. J. Chem. Tech. Biotechnol. 49, 285-295.

Henze, M., Gujer, W., Mino, T., Van Loosdrecht, M.C.M., 2000. Activated Sludge Models ASM1, ASM2, ASM2d and ASM3. Scientific and Technical Report Nº9, IWA Publishing, London.

Hill, R.W., Wyse, G.A., Anderson, M., 2012. Animal Physiology. Sinauer Associates Inc., Ed.3, Sunderland, MA.

Hukkerikar, A.S., Meier, R., Sin, Gürkan, Gani, R., 2013. A method to estimate the enthalpy of formation of organic compounds with chemical accuracy. Fluid Phase Equilibria Volume 348(25), 23-32.

Inoije, S., Sawayama, S., Ogi, T., Yokoyama, S.Y., 1996. Organic Composition of Liquidized Sewage Sludge. Biomass and Bioenergy. 10, 37–40.Jeppsson U., Pons M.N., Nopens I., Alex J., Copp J.B., Gerneay K.V., Rosen C., Steyer J.P., Vanrolleghem P.A., 2007. Benchmark simulation model No 2 – general protocol and exploratory case studies. Wat. Sci. Tech., 53(8), 67-78.

Jewell W.J., 1982. Autoheated Aerobic Thermophilic Digestion with Air Aeration. EPA project No. R 804636, MERL Report, NTIS PB-82-196908.

la Cour Jansen, J., Kristensen, G.H., Laursen, K.D., 1992. Activated sludge nitrification in temperate climate. Water Sci. Technol. 25(4–5), 177–184.

Lapara, T.M., Alleman, J.E., 1999. Thermophilic aerobic biological wastewater treatment. *Water Research*, 33(4), 895-908.

Lebedeva, N.D., 1964. Heats of combustion of monocarboxylic acids, Russ. J. Phys. Chem. (Engl. Transl.), 38, 1435-1437.

Lippi, S., Rosso, D., Lubello, C., Canziani, R., Strenstrom, M., 2009. Temperature modelling and prediction for activated sludge systems. Water Science and Technology 59, pp 125-131.

Makinia, J., Scott, A., Zima, P., 2005. Temperature modeling in activated sludge systems - A case study. Water Environ. Res. 77, 525–532.

Masterton, W.L., Hurley, C.N., 2003. Química. Principios y Reacciones. Ediciones Paraninfo, Ed 4. Madrid.

McCarty P.L., 1972. Energetics of organic matter degradation. Water Pollution Microbiology, R. Mitchell Ed., Wiley-Interscience, NY.

Messenger, J.R., Ekama, G.A., 1993. Evaluation of the dual digestion system: Part 4 - Simulation of the temperature profile in the batch fed aerobic reactor. Water SA, 19(3) 209-215.

Messenger, J.R., Ekama, G.A., de Villiers, H.A., Kenmuir, K., Laubscher, S.A., 1992. Evaluation and optimisation of dual digestion of sewage sludge – Part 2: Aerobic reactor performance. Final report WRC 189/3/92. Water Research Commission, PO Box 824. Pretoric, 0001.

Messenger, J.R., de Villiers, H.A., Ekama, G.A., 1990. Oxygen utilization rate as a control parameter for the aerobic stage in dual digestion. Wat. Sci. Tech., 22(12) 217-227.

Metcalf & Eddy., 2004. Wastewater Engineering, Treatment Disposal and. Reuse, 4th Edition. Singapore, Mcgraw-Hill. Mosely, F.E., and Hughes, D.A. 1975.

National Institute of Standards and Technology, NIST. http://www.nist.gov

Nelson, L.D., Cox, M.M., 2005. Lehninger, Principles of biochemistry. N. H. Freeman, Ed. 4, New York.

Novotny, V., Krenkel, P. 1973. Evaporation and heat balance in aerated basins. AIChE Symp. Series, Water 70(136), 150–159.

Oh, S.T., Martin, A.D., 2010. Long chain fatty acids degradation in anaerobic digester: Thermodynamic equilibrium consideration. Process Biochemistry. 45(3): 335-345.

Oh, S.T., Martin, A.D., 2007. Thermodynamic Equilibrium Model in anaerobic digestion process. Biochemical Engineering Journal. 34(3): 256-266.

Paul, P., 2013. Assessing the influence of pronounced diurnal temperature variations in nontemperate zones on the denitrification/nitrification rate using the COST Benchmark activated sludge model no. 1 simulation. Water and Environmental Journal. Print ISSN 1747-6585.

Perry, R.H., Green, D.W., 1999. Perry´s “Chemical Engineer´s Handbook”, McGraw-Hill, USA.

Pitt, A.J., Ekama, G.A., 1996. Dual digestion of sewage sludge with air and pure oxygen. Procs 69th Water Environment Federation Annual conference and exhibition, Dallas TX, 2, 69-82.

Pitt, A.J., Ekama, G.A., 1995. The dual digestion of sewage sludge using air and pure oxygen. UCT Report No 87/1995, Dept. of Eng., Univ. of Cape Town, Rondebosch, Cape, RSA.

Prochazka, G.J., Payne, W.J., Mayberry, W.R., 1973. Calorific Contents of Microorganisms. Biotechnology and Bioengineering, Vol.XV, 1007-1010.

Reger, D.L., Goode, S.L., Ball, D.W., 2010. Chemistry: Principles and Practice. Ed. 3. Chemistry Department Books. Bedford. CA.

Reichert, P., Borchardt D., Henze M., Rauch W., Shanahan P., Somlyódy L. and Vanrolleghem P., 2001. River Water Quality Model Nº1. Scientific and Technical Report Nº12, IWA Publishing, London.

Riley, D.W., and Forster, C.F., 2002. An evaluation of an autothermal aerobic digestion system. Transactions of the Institution of Chemical Engineers, Part B - Process Safety and Env. Protection, 80B . pp. 100-104.Sethi, G., Kumar, D., Sarna, J., Maurya, L., Ram, R.B., 2011. Future of water treatment: Membrane bioreactor technology. IPPTA J. 4, 145-149.

Sedory, P.E., Stenstrom, M.K., 1995. Dynamic prediction of wastewater aeration basin temperature. Journal of Environmental Engineering. 121, 609-618.

Shizas, I,, Bagley, D.M., 2004. Experimental Determination of Energy Content of Unknown Organics in Municipal wastewater Streams. Journal of Energy Engineering. 130(2):45-53.

Steele, W.V., Chirico, R.D., Cowell, A.B., Knipmeyer, S.E., Nguyen, A., 1997. Thermodynamic properties and ideal-gas enthalpies of formation for 2-aminoisobutyric acid (2-methylalanine), acetic acid, (4-methyl-3-penten-2-one), 4-methylpent-1-ene, 2,2'-bis(phenylthio)propane, and glycidyl phenyl ether (1,2-epoxy-3-phenoxypropane). J. Chem. Eng. Data, 42, 1052-1066.

van Hulle, S.W.H., vandeweyer, H.J.P., Meesschaert, B.D., Vanrolleghem, P.A., Dejans, P., Dumoulin, A., 2010. Engineering aspects and practical application of autotrophic nitrogen removal from nitrogen rich streams, Chem. Eng. J., 162, 1–20.

Vismara, R., 1985. A model for autothermic aerobic digestion. Wat. Res. 19, 441-447.

Zanoni, A.E., Mueller, D.L., 1982. Calorific value of wastewater plant sludge. J. Environ. Eng. Div. (Am. Soc. Civ. Eng.). 108(1), 187-195.

Table 1 - Gas phase formation enthalpies

i	Name	Formula	Description	Δhf^{o}_{g} (kJ mol^{-1})	Δhf^{o}_{g} (kJ g$_{stoich.\ unit}^{-1}$)	Reference
1	G_{CO2}	CO_2	Carbon dioxide	-393.51	-32.79 kJ g_C^{-1}	Perry & Green (1999)
2	G_{H2}	H_2	Hydrogen	0.00	0.00 kJ g_{COD}^{-1}	Perry & Green (1999)
3	G_{CH4}	CH_4	Methane	-74.80	-1.17 kJ g_{COD}^{-1}	Perry & Green (1999)
4	G_{NH3}	NH_3	Ammonia	-45.90	-3.28 kJ g_N^{-1}	Perry & Green (1999)
5	G_{N2}	N_2	Nitrogen	0.00	0.00 kJ g_N^{-1}	Perry & Green (1999)
6	G_{O2}	O_2	Oxygen	0.00	0.00 kJ g_{O2}^{-1}	Perry & Green (1999)
7	G_{H2O}	H_2O	Water steam	-241.81	-13.43 kJ g_{H2O}^{-1}	Perry & Green (1999)

Table 2 - Water phase formation enthalpies

i	Name	Formula	Description	Δhf °$_w$ (kJ mol^{-1})	Δhf °$_w$ (kJ g $_{stoich. unit}^{-1}$)	Reference
1	S_{H20}	H_2O	Water steam	-285.84	-15.88 kJ g_{H2O}^{-1}	Perry & Green (1999)
2	S_{02}	O_2	Dissolved Oxygen	0.00	0.00 kJ g_{O2}^{-1}	Perry & Green (1999)
3	S_H^+	H^+	Protons	0.00	0.00 kJ g_H^{-1}	Brown *et al.* (1993)
4	S_{OH}^-	OH^-	Hydroxide ions	-230.00	-230.00 kJ g_H^{-1}	Brown *et al.* (1993)
5	$S_{HPO4=}$	$(HPO_4)^=$	Hydroxy phosphate	-1298.70	-41.89 kJ g_P^{-1}	Chang (1999)
6	S_{H2PO4-}	$(H_2PO_4)^-$	Dihydroxy	-1302.48	-42.01 kJ g_P^{-1}	Chang (1999)
7	S_{NH4+}	$(NH_4)^+$	Ammonium	-132.50	-9.46 kJ g_N^{-1}	Brown *et al.* (1993)
8	S_{NH3}	NH_3	Ammonia	-80.29	-5.73 kJ g_N^{-1}	Brown *et al.* (1993)
9	S_{CO2}	CO_2	Dis.Carbon dioxide	-412.90	-34.41 kJ g_C^{-1}	Chang (1999)
10	S_{HCO3-}	$(HCO_3)^-$	Bicarbonate	-691.10	-57.59 kJ g_C^{-1}	Chang (1999)
11	S_{SU}	$C_6H_{12}O_6$	Monosaccharides	-1268.20	-6.61 kJ g_{COD}^{-1}	Reger *et al.* (2010)
12	S_{AA}	$C_4H_{6.1}0_{1.2}N$	Amino acids	-306.10	-2.29 kJ g_{COD}^{-1}	NIST
13	S_{FA}	$C_{16}O_2H_{32}$	LCFAs	-848.40	-1.15 kJ g_{COD}^{-1}	Lebedeva (1964)
14	S_{HVA}	$C_5H_{10}O_2$	Valeric acid	-558.90	-2.69 kJ g_{COD}^{-1}	Adriaanse *et al.* (1965)
15	S_{VA-}	$C_5H_9O_2^-$	Valerate	-501.07~~-~~	-2.41~~28~~ kJ g_{COD}^{-1}	~~Constantinou *et al.* (1994)~~Hukkerikar *et al.*, 2013
16	S_{HBU}	$C_4H_8O_2$	Butyric acid	-533.92	-3.34 kJ g_{COD}^{-1}	Lebedeva (1964)
17	S_{BU-}	$C_4H_7O_2^-$	Butyrate	-519.20	-3.25 kJ g_{COD}^{-1}	Everett *et al.* (1939)
18	S_{HPRO}	$C_3H_6O_2$	Propionic acid	-510.80	-4.56 kJ g_{COD}^{-1}	Lebedeva (1964)
19	S_{PRO-}	$C_3H_5O_2^-$	Propionate	-507.79	-4.53 kJ g_{COD}^{-1}	Everett *et al.* (1939)
20	S_{HAC}	$C_2H_4O_2$	Acetic acid	-483.52	-7.56 kJ g_{COD}^{-1}	Steele *et al.* (1997)
21	S_{AC-}	$C_2H_3O_2^-$	Acetate	-482.09	-7.53 kJ g_{COD}^{-1}	Everett *et al.* (1939)
22	S_{H2}	H_2	Hydrogen	0.00	0.00 kJ g_{COD}^{-1}	Perry & Green (1999)
23	S_{CH4}	CH_4	Dis. Methane	-82.97	-1.30 kJ g_{COD}^{-1}	NIST
24	S_{N2}	N_2	Dis. Nitrogen	0.00	0.00 kJ g_N^{-1}	Perry & Green (1999)
25	S_{NO2-}	NO_2^-	Nitrites	-104.60	-7.47 kJ g_N^{-1}	Masterton & Hurley (2003)
26	S_{HNO2}	HNO_2	Nitrous acid	-116.00	-8.29 kJ g_N^{-1}	Guillaumont *et al.* (2003)
27	S_{NO3-}	$(NO_3)^-$	Nitrates	-206.57	-14.76 kJ g_N^{-1}	Chang (1999)
28	S_I	$C_7H_{9.1}O_{2.65}NP_{0.05}$	Soluble Inerts	-495.00	-1.34 kJ g_{COD}^{-1}	Need estimation
29	S_P	$C_7H_{9.1}O_{2.65}NP_{0.05}$	Lysis sol. Product	-495.00	-1.34 kJ g_{COD}^{-1}	Need estimation
30	X_{C1}	$C_{13.7}H_{24}O_{3.8}N_{0.5}P_{0.035}$	Composites	-555.90	-1.94 kJ g_{COD}^{-1}	Need estimation
31	X_{C2}	$C_5H_{6.9}O_2NP_{0.1}$	Decay complex	-414.02	-2.54 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
32	X_{CH}	$C_6H_{9.95}O_5P_{0.05}$	Carbohydrates	-979.00	-5.06 kJ g_{COD}^{-1}	Brown (2011)
33	X_{PR}	$(C_4H_{6.1}O_{1.2}N)_x$	Proteins	-284.10	-2.13 kJ g_{COD}^{-1}	Nelson *et al.*, (2005)
34	X_{LI}	$C_{51}H_{97.9}O_6P_{0.1}$	Lipids	-2474.17	-1.06 kJ g_{COD}^{-1}	Freedman *et al.* (1989)
35	X_H	$C_5H_{6.9}O_2NP_{0.1}$	Heterotrophic bac.	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
36	X_{AOB}	$C_5H_{6.9}O_2NP_{0.1}$	Nitrosomona bac.	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
37	X_{NOB}	$C_5H_{6.9}O_2NP_{0.1}$	Nitrobacter bac.	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
38	X_{SU}	$C_5H_{6.9}O_2NP_{0.1}$	Sugar degrader bac.	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
39	X_{AA}	$C_5H_{6.9}O_2NP_{0.1}$	Amino-acid	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
40	X_{FA}	$C_5H_{6.9}O_2NP_{0.1}$	LCFA degrader bac.	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
41	X_{C4}	$C_5H_{6.9}O_2NP_{0.1}$	Val/but degrader	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
42	X_{PRO}	$C_5H_{6.9}O_2NP_{0.1}$	Propionate degrader	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
43	X_{AC}	$C_5H_{6.9}O_2NP_{0.1}$	Acetate degrader	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
44	X_{H2}	$C_5H_{6.9}O_2NP_{0.1}$	Hydrogen degrader	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
45	X_{AN}	$C_5H_{6.9}O_2NP_{0.1}$	Anammox bac.	-414.02	-2.537 kJ g_{COD}^{-1}	Prochazka *et al.* (1973)
46	X_I	$C_7H_{9.1}O_{2.65}NP_{0.05}$	Particulate inert	-718.41	-3.11 kJ g_{COD}^{-1}	Need estimation
47	X_P	$C_7H_{9.1}O_{2.65}NP_{0.05}$	Lysis particulate	-718.41	-3.11 kJ g_{COD}^{-1}	Need estimation

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48	X_{II}	X	Inorganic inert	-	-	-

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

	Term	Description	Equations
Input / Output due to Transformations	$\overline{H}_{g1,g2}$	Enthalpy lost/gained by the 1st gaseous phase due to transformation (from/to the 2nd gaseous phase)	$\left(\widetilde{E}^{T}_{g1,g2}\overline{\rho}_{g1,g2}\right)_i \left[\left(Cp_{g1}\right)_i\left(T_{g1}-\left(T_{g1,ref}\right)_i\right)+\left(h_{g1,ref}\right)_i\right]$
	$\overline{H}_{g1,w}$	Enthalpy lost/gained by the 1st gaseous phase due to transformation (from/to the aqueous phase)	$\left(\widetilde{E}^{T}_{g1,w}\overline{\rho}_{g1,w}\right)_i \left[\left(Cp_{g1}\right)_i\left(T_{g1}-\left(T_{g1,ref}\right)_i\right)+\left(h_{g1,ref}\right)_i\right]$
	$\overline{H}_{g2,g1}$	Enthalpy lost/gained by the 2nd gaseous phase due to transformation (from/to the 1st gaseous phase)	$\left(\widetilde{E}^{T}_{g2,g1}\overline{\rho}_{g2,g1}\right)_i \left[\left(Cp_{g2}\right)_i\left(T_{g2}-\left(T_{g2,ref}\right)_i\right)+\left(h_{g2,ref}\right)_i\right]$
	$\overline{H}_{g2,w}$	Enthalpy lost/gained by the 2nd gaseous phase due to transformation (from/to the aqueous phase)	$\left(\widetilde{E}^{T}_{g2,w}\overline{\rho}_{g2,w}\right)_i \left[\left(Cp_{g2}\right)_i\left(T_{g2}-\left(T_{g2,ref}\right)_i\right)+\left(h_{g2,ref}\right)_i\right]$
	$H_{w,g1}$	Enthalpy lost/gained by the aqueous phase due to transformation (from/to the 1st gaseous phase)	$\left(\widetilde{E}^{T}_{w,g1}\overline{\rho}_{w,g1}\right)_{H2O} \left[Cp_{w,H2O}\left(T_w-T_{w,ref,H2O}\right)+h_{w,ref,H2O}\right]$
	$H_{w,g2}$	Enthalpy lost/gained by the aqueous phase due to transformation (from/to the 2nd gaseous phase)	$\left(\widetilde{E}^{T}_{w,g2}\overline{\rho}_{w,g2}\right)_{H2O} \left[Cp_{w,H2O}\left(T_w-T_{w,ref,H2O}\right)+h_{w,ref,H2O}\right]$
Input	$H_{w,in}$	Enthalpy associated with the aqueous influent	$\left[Cp_{w,H2O}\left(T_{w,in}-T_{w,ref,H2O}\right)+h_{w,ref,H2O}\right]\left(\dot{m}_{w,in}\right)_{H2O}$
	$\overline{H}_{g,in}$	Enthalpy associated with the gaseous influent	$\left[\left(Cp_{g2}\right)_i\left(T_{g2,in}-\left(T_{g2,ref}\right)_i\right)+\left(h_{g2,ref}\right)_i\right]\left(\dot{m}_{g,in}\right)_i$
Output	$H_{w,out}$	Enthalpy associated with the aqueous effluent	$\left[Cp_{w,H2O}\left(T_w-T_{w,ref,H2O}\right)+h_{w,ref,H2O}\right]\left(\dot{m}_{w,out}\right)_{H2O}$
	$\overline{H}_{g,in}$	Enthalpy associated with the gaseous effluent	$\left[\left(Cp_{g1}\right)_i\left(T_{g1}-\left(T_{g1,ref}\right)_i\right)+\left(h_{g1,ref}\right)_i\right]\left(\dot{m}_{g,out}\right)_i$
Conduction / Convection	H_{phs1}	Enthalpy flow transfer between the water and the 1st gaseous phase	$\dfrac{\alpha_{phs,g1}\left(Gr\ Pr\right)^{n_{phs,g1}}\left(\overline{k}_{g1}\ \overline{X}^{T}_{g1}\right)\left(T_w-T_{g1}\right)A_{tank}}{\delta}$ where, $Gr=\dfrac{g\ \beta_{phs}\left(T_w-T_{med}\right)\delta^3}{\left(\overline{\upsilon}_{med}\ \overline{X}^{T}_{med}\right)^2}$ $Pr=\dfrac{\left(\overline{\mu}_{med}\ \overline{X}^{T}_{med}\right)\left(\overline{Cp}_{med}\ \overline{X}^{T}_{med}\right)}{\left(\overline{k}_{med}\ \overline{X}^{T}_{med}\right)}$
	H_{phs2}	Enthalpy flow transfer between the water and the 2nd gaseous phase	$\dfrac{\alpha_{phs,g2}\left(Gr\ Pr\right)^{n_{phs,g2}}\left(\overline{k}_{g2}\ \overline{X}^{T}_{g2}\right)\left(T_w-T_{g2}\right)A_{bubbles}}{\delta}$
	$H_{gc,out}$	Enthalpy lost/gained through walls and pipes by conduction (gaseous phase)	$k_{wls}\left(T_w-T_{atm}\right)A_w$
	$H_{wc,out}$	Enthalpy lost/gained through walls and pipes by conduction (aqueous phase)	$k_{wls}\left(T_{g1}-T_{atm}\right)A_g$
Radiation	$H_{atm,rad,g}$	Longwave atmospheric radiation flux (gaseous phase)	$k_{SB}\ A_g\left[\varepsilon_{atm}\left(T_{g1}{}^{*}\right)^4-(1-\lambda_{atm})\beta_{air}\left(T_{atm}{}^{*}\right)^4\right]$
	$H_{atm,rad,w}$	Longwave atmospheric radiation flux (aqueous phase)	$k_{SB}\ A_w\left[\varepsilon_{atm}\left(T_w{}^{*}\right)^4-(1-\lambda_{atm})\beta_{air}\left(T_{atm}{}^{*}\right)^4\right]$
	$H_{sol,rad,g}$	Shortwave solar radiation flux (gaseous phase)	$\alpha_{rad}\ k_{sol,rad}\ A_g$
	$H_{sol,rad,w}$	Shortwave solar radiation flux (aqueous phase)	$\alpha_{rad}\ k_{sol,rad}\ A_w$
Actuator	$H_{m,in}$	Enthalpy transmitted from the actuators (mechanical)	$P_m\left(1-\eta_m\right)$

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

	Reaction	**Δh^o_r**		**Reference**
		Model	Literature	
1	Substrate (aq.) + xO_2(g) → yH_2O(l) + zCO_2(g)+Biomass	13.62 – 14.62 kJ/gCOD$_{\text{rem.}}$	12.28 – 16.46 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Cooney *et al.*, 1968
			13.32 – 15.12 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Andrews and Kambhu, 1969
			14.30 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	McCarty, 1972
			13.5 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Zanoni and Mueller, 1982
			12.50 – 16.66 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Jewell, 1982
			13.6 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Heinritz *et al.*, 1990
			12.1 – 13.7 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Messenger *et al.*, 1992
			12.8 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Pitt *et al.*, 1995
			15.68 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Riley and Forster, 2002
			12.4 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Shizas and Bagley, 2004
			13.9 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Gomez *et al.*, 2007
			17.8 kJ/gCOD$_{\text{rem.}}$ $^{(E)}$	Heidrich *et al.*, 2011
2	$C_6H_{12}O_6$(aq.)+3O_2(g) →3H_2O(l) +3CO_2(g)+Biomass	-893.1 kJ/mol$_{\text{SSU rem}}$	-890.0 kJ/mol$_{\text{SSU rem.}}$ $^{(T)}$	Gallert *et al.*, 2005
3	NH_4^+ (aq.)+1.5 O_2 (g) → 2H^+(aq.) + NO_2^- (aq.)+H_2O (l)	-258.0 kJ/mol$_{\text{N rem.}}$	-259.0 kJ/mol$_{\text{N rem.}}$ $^{(T)}$	Daverio *et al.*, 2003
4	NO_2^- (aq.)+0.5 O_2 (g) → NO_3^- (aq.)	-102.0 kJ/mol$_{\text{N rem.}}$	-99.4 kJ/mol$_{\text{N rem.}}$ $^{(T)}$	Daverio *et al.*, 2003
5	NH_4^+ (aq.)+NO_2^- (aq.) → N_2 (g)+ 2H_2O (l)	-334.6 kJ/mol$_{\text{N rem.}}$	-333.0 kJ/mol$_{\text{N rem.}}$ $^{(T)}$	Buttiglieri *et al.*, 2010
6	$C_6H_{12}O_6$(aq.)→ 2.85CH_4(g) + 2.85CO_2(g)	-132.8 kJ/mol$_{\text{SSU rem.}}$	-131.0 kJ/mol$_{\text{SSU rem.}}$ $^{(T)}$	Gallert *et al.*, 2005
7	CH_3COOH(aq.)→ CH_4(aq.) + CO_2(aq.)	-12.4 kJ/mol$_{\text{SHAC rem.}}$	-15.3 kJ/mol$_{\text{SHAC rem.}}$ $^{(T)}$	Oh *et al.*, 2007
8	CH_3COOH(aq.)→ CH_4(g) + CO_2(aq.)	-4.8 kJ/mol$_{\text{SHAC rem.}}$	$\Delta h^o_r < 0$ $^{(T)}$	Oh *et al.*, 2007
9	CH_3COOH(aq.)→ CH_4(g) + CO_2(g)	15.2 kJ/mol$_{\text{SHAC rem.}}$	$\Delta h^o_r > 0$ $^{(T)}$	Oh *et al.*, 2007
10	HAC digestion (aq.) (methanogenesis)	-9.8 kJ/mol$_{\text{SHAC rem.}}$	$\Delta h^o_r < 0$ $^{(T)}$	Oh *et al.*, 2010
11	HPRO digestion (aq.) (acetogenesis & methanogenesis)	0.6 kJ/mol$_{\text{SHPRO rem.}}$	$\Delta h^o_r > 0$ $\Delta h^o_{r,11} > \Delta h^o_{r,10}$ $^{(T)}$	Oh *et al.*, 2010
12	HBU digestion (aq.) (acetogenesis & methanogenesis)	6.8 kJ/mol$_{\text{SHBU rem.}}$	$\Delta h^o_r > 0$ $\Delta h^o_{r,12} > \Delta h^o_{r,11}$ $^{(T)}$	Oh *et al.*, 2010
13	HVA digestion (aq.) (acetogenesis & methanogenesis)	16.9 kJ/mol$_{\text{SHVA rem.}}$	$\Delta h^o_r > 0$ $^{(T)}$ $\Delta h^o_{r,13} > \Delta h^o_{r,12}$ $^{(T)}$	Oh *et al.*, 2010

Theoretical $^{(T)}$ and Experimental Data $^{(E)}$

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}
Oxidation heats (kJ/gCOD $_{rem.}$)	-15.23	-14.38	-14.64	-14.11	-14.13	-14.16	-14.28
Oxidation + CO_2 stripping heats (kJ/gCOD $_{rem.}$)	-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^{3}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

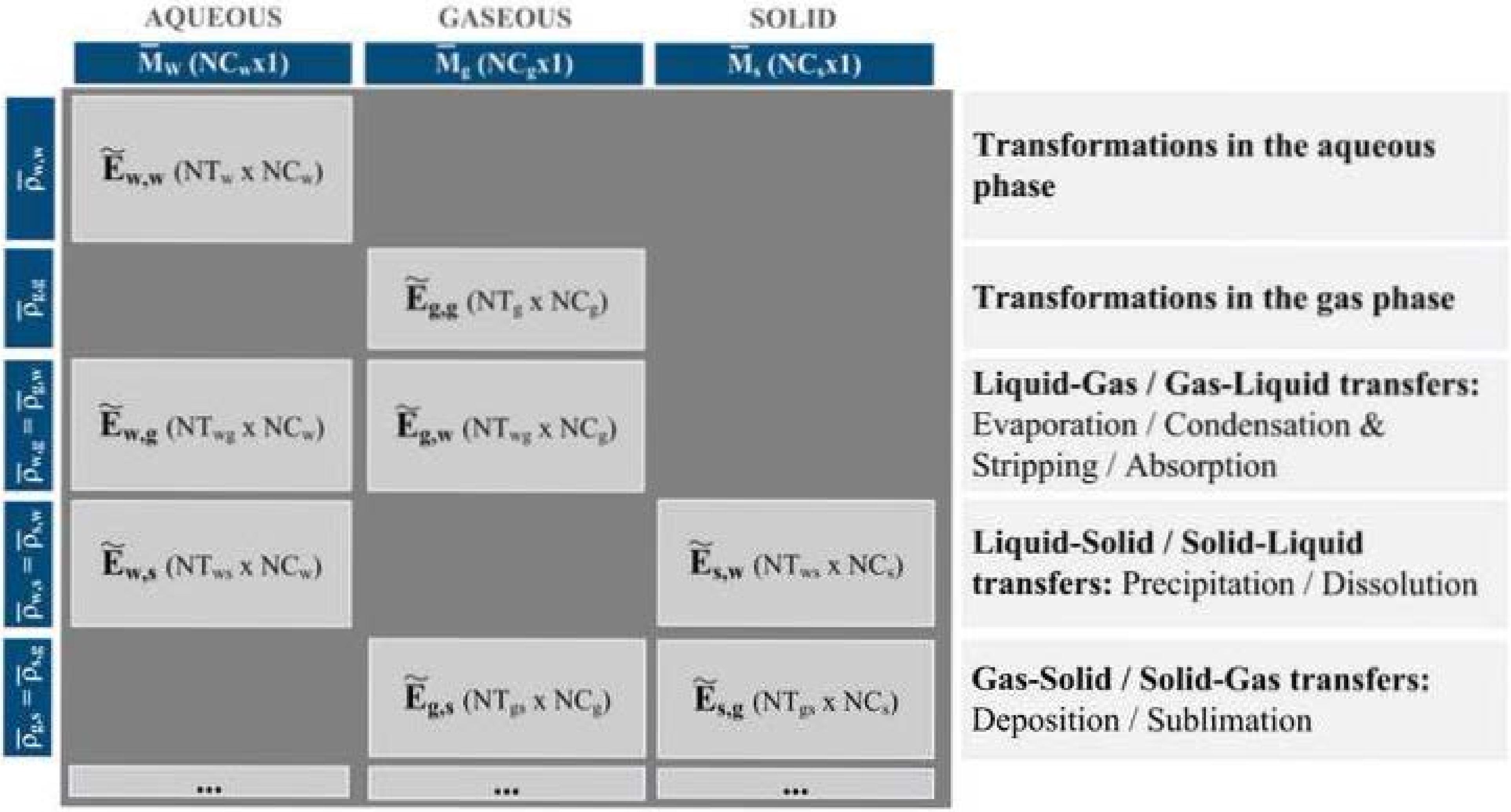
Figure 3 - Schematic representation of the enthalpy balance in a C-CSTR

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

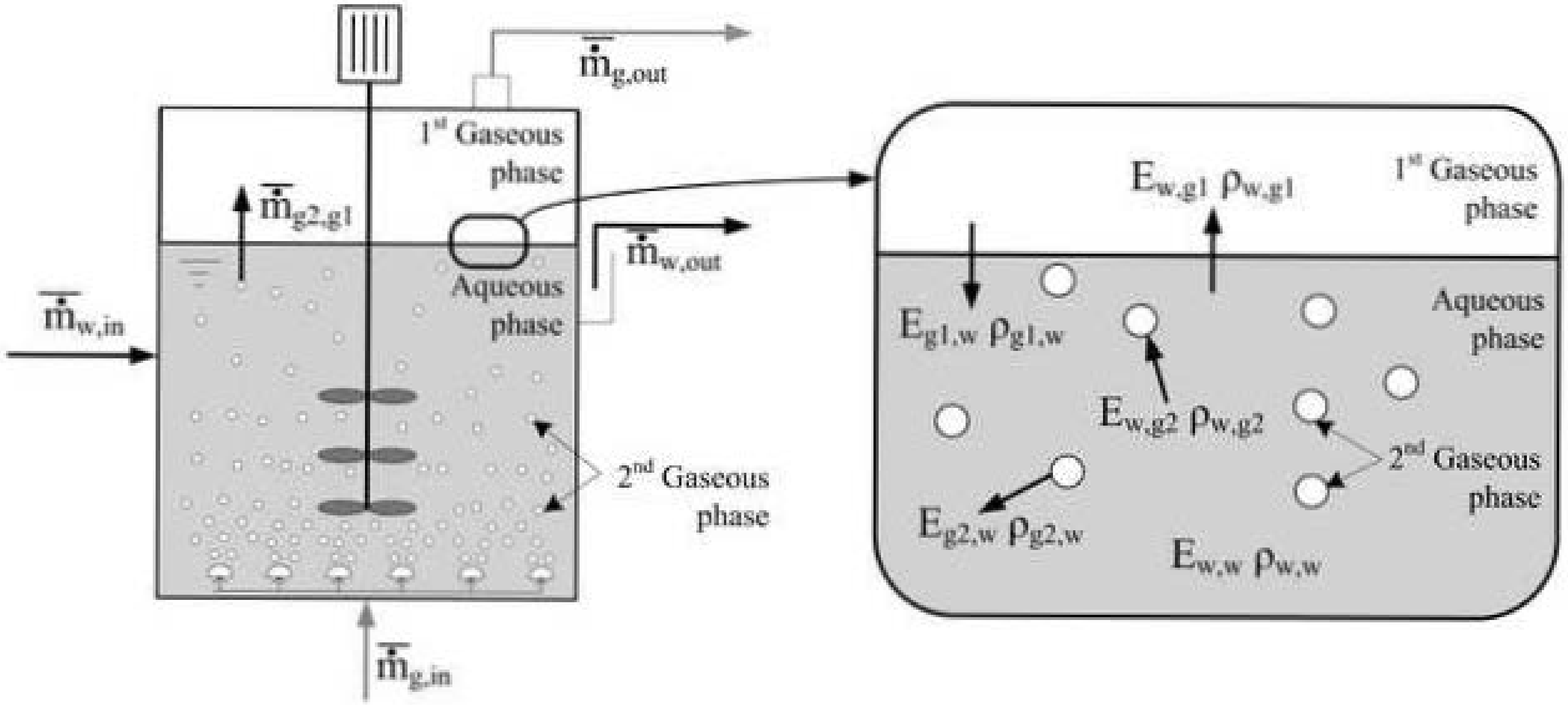
Figure 5 – (a) Experimental and simulation results for the full scale ATAD, (b) Total enthalpy produced and consumed in the system with the contribution of each thermal flux

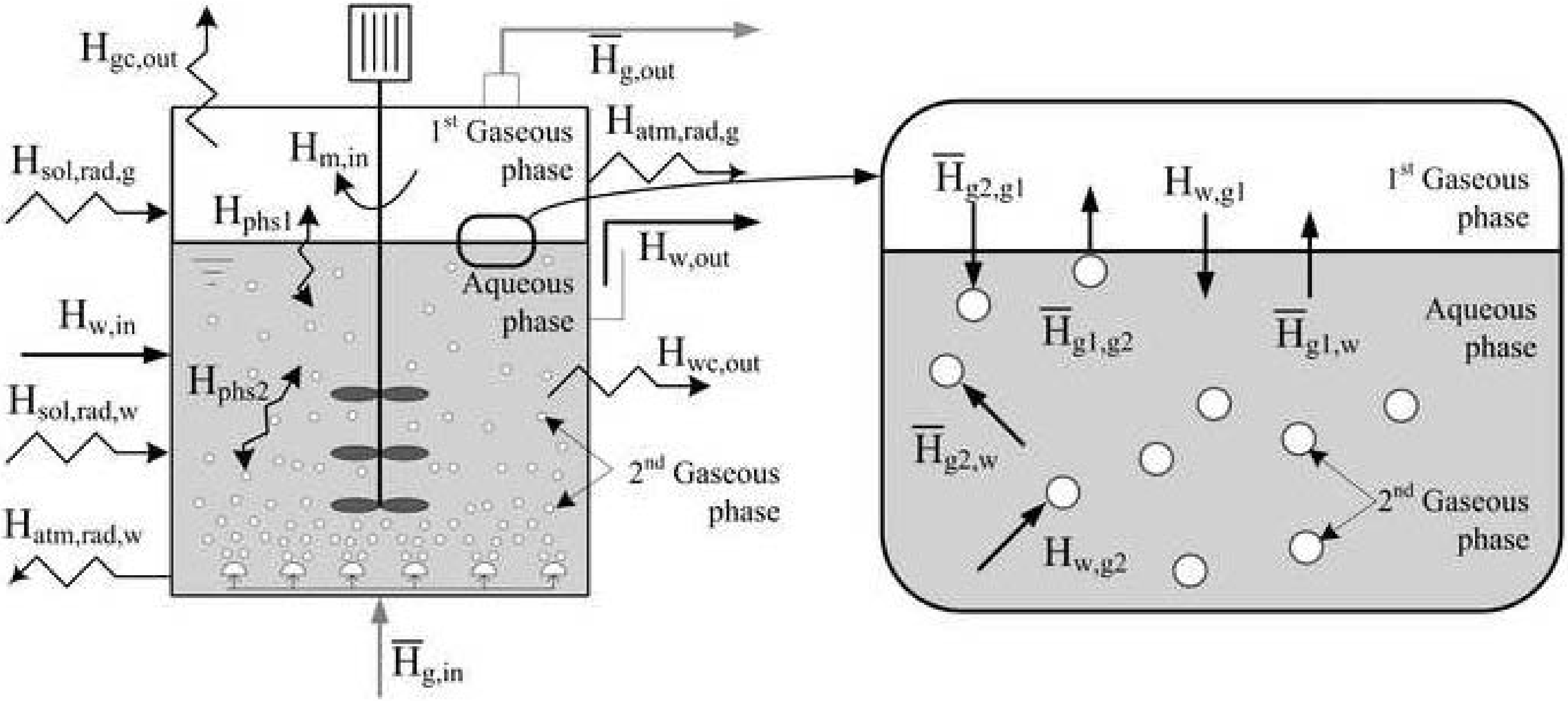
Figure 6 – Behaviour of the temperature in a full scale ATAD for constant OLR and variable aeration flows

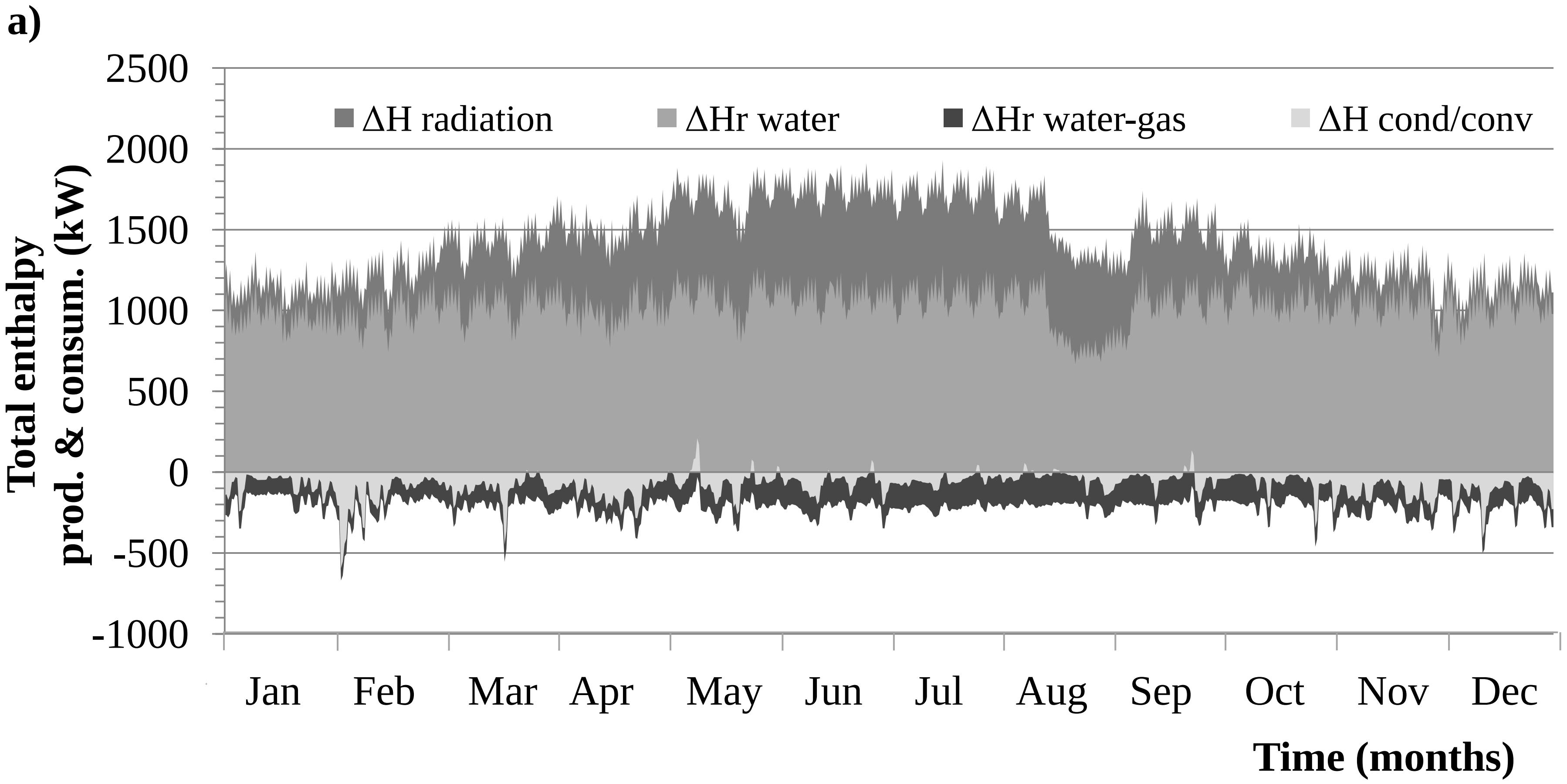
Figure 7 – (a) Temperature evolution for different influent characterizations (b) Aqueous transformation heats (specific heat yield) for different influent characterizations

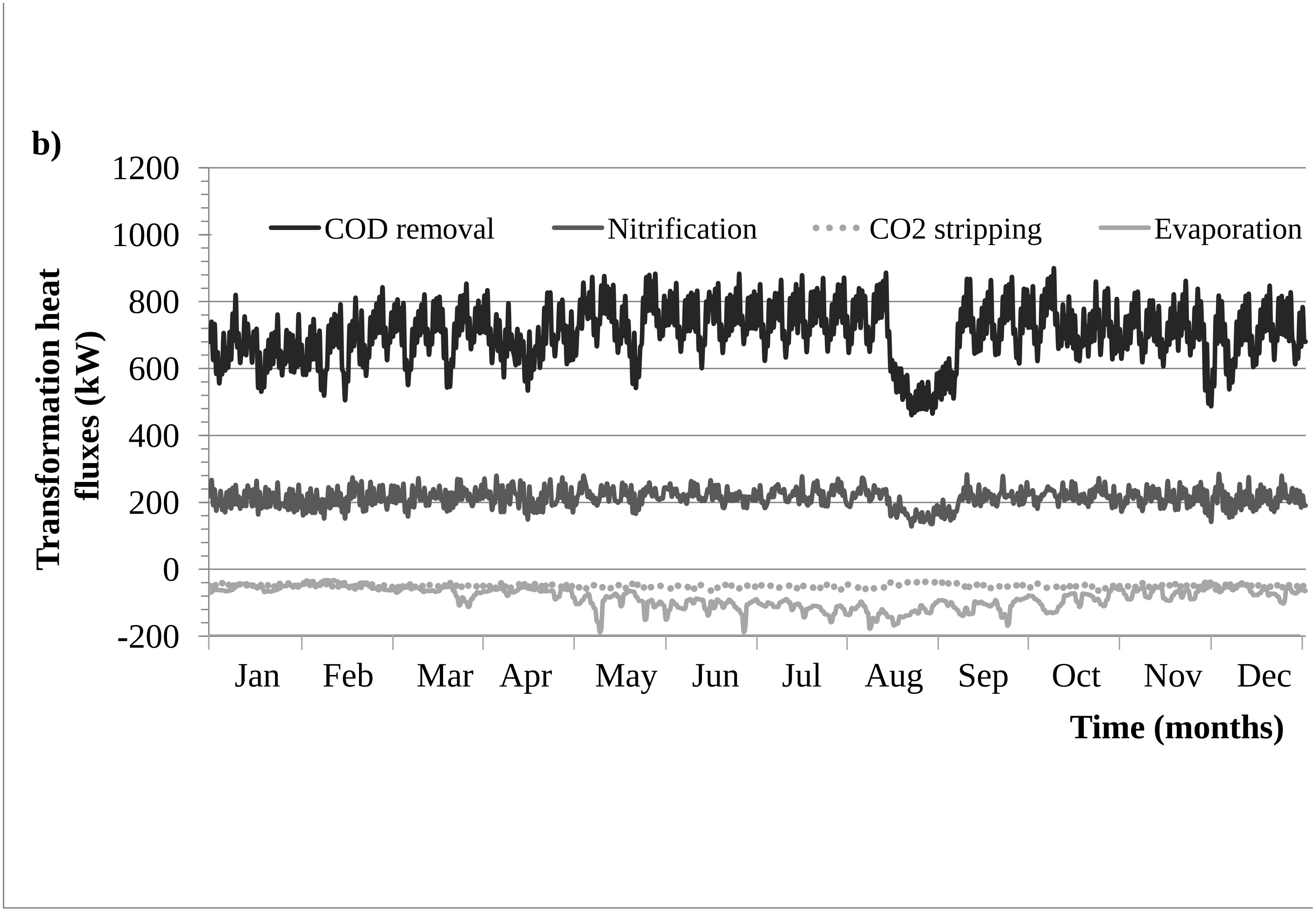


	AQUEOUS $\overline{M}_W$ (NC_wx1)	GASEOUS $\overline{M}_g$ (NC_gx1)	SOLID $\overline{M}_s$ (NC_sx1)	
$\overline{\rho}_{w,w}$	$\widetilde{\mathbf{E}}_{\mathbf{w,w}}$ (NT_w x NC_w)			**Transformations in the aqueous phase**
$\overline{\rho}_{g,g}$		$\widetilde{\mathbf{E}}_{\mathbf{g,g}}$ (NT_g x NC_g)		**Transformations in the gas phase**
$\overline{\rho}_{w,g} = \overline{\rho}_{g,w}$	$\widetilde{\mathbf{E}}_{\mathbf{w,g}}$ (NT_{wg} x NC_w)	$\widetilde{\mathbf{E}}_{\mathbf{g,w}}$ (NT_{wg} x NC_g)		**Liquid-Gas / Gas-Liquid transfers:** Evaporation / Condensation & Stripping / Absorption
$\overline{\rho}_{w,s} = \overline{\rho}_{s,w}$	$\widetilde{\mathbf{E}}_{\mathbf{w,s}}$ (NT_{ws} x NC_w)		$\widetilde{\mathbf{E}}_{\mathbf{s,w}}$ (NT_{ws} x NC_s)	**Liquid-Solid / Solid-Liquid transfers:** Precipitation / Dissolution
$\overline{\rho}_{g,s} = \overline{\rho}_{s,g}$		$\widetilde{\mathbf{E}}_{\mathbf{g,s}}$ (NT_{gs} x NC_g)	$\widetilde{\mathbf{E}}_{\mathbf{s,g}}$ (NT_{gs} x NC_s)	**Gas-Solid / Solid-Gas transfers:** Deposition / Sublimation
	...	...	...	

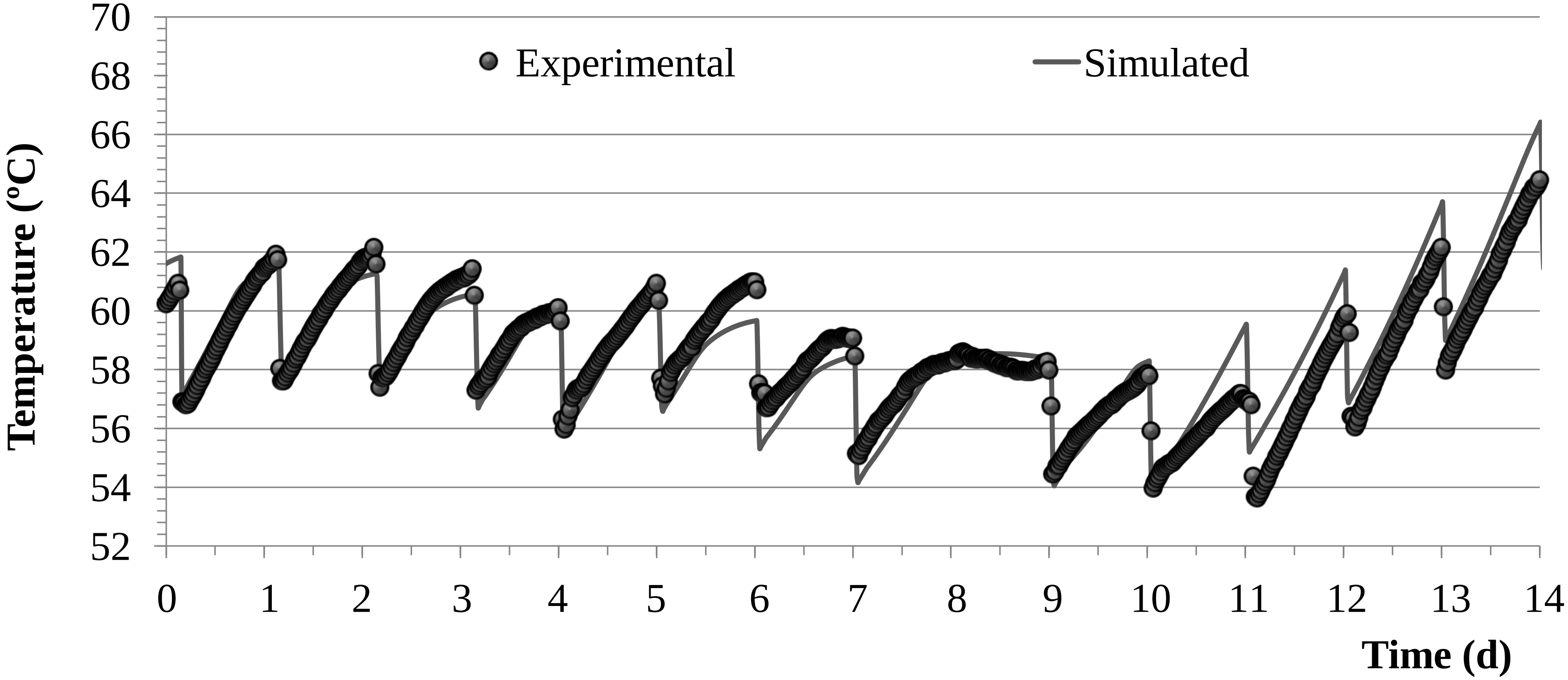

$\bar{\dot{m}}_{g,out}$
1st Gaseous phase
$\bar{\dot{m}}_{g2,g1}$
$\bar{\dot{m}}_{w,out}$
Aqueous phase
$\bar{\dot{m}}_{w,in}$
2nd Gaseous phase
$\bar{\dot{m}}_{g,in}$
$E_{w,g1}$ $\rho_{w,g1}$
1st Gaseous phase
$E_{g1,w}$ $\rho_{g1,w}$
Aqueous phase
$E_{w,g2}$ $\rho_{w,g2}$
2nd Gaseous phase
$E_{g2,w}$ $\rho_{g2,w}$
$E_{w,w}$ $\rho_{w,w}$


$H_{gc,out}$
$\overline{H}_{g,out}$
$H_{m,in}$
1st Gaseous phase
$H_{atm,rad,g}$
$H_{sol,rad,g}$
H_{phs1}
$H_{w,out}$
Aqueous phase
$H_{w,in}$
$H_{wc,out}$
H_{phs2}
$H_{sol,rad,w}$
2nd Gaseous phase
$H_{atm,rad,w}$
$\overline{H}_{g,in}$
$\overline{H}_{g2,g1}$
$H_{w,g1}$
1st Gaseous phase
Aqueous phase
$\overline{H}_{g1,g2}$
$\overline{H}_{g1,w}$
$\overline{H}_{g2,w}$
$H_{w,g2}$
2nd Gaseous phase

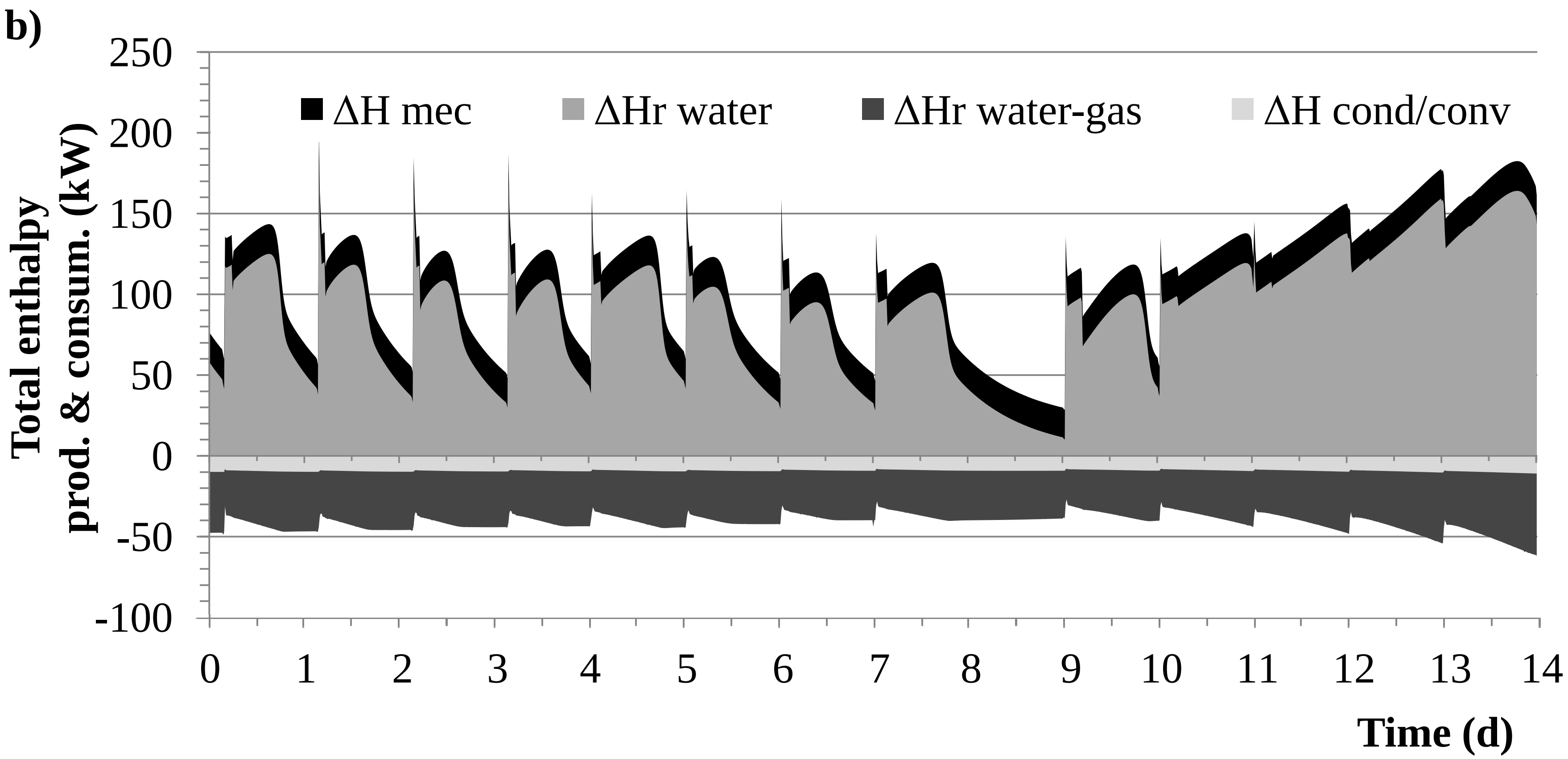

a)
ΔH radiation
ΔHr water
ΔHr water-gas
ΔH cond/conv
Total enthalpy
prod. & consum. (kW)
2500
2000
1500
1000
500
0
-500
-1000
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Time (months)

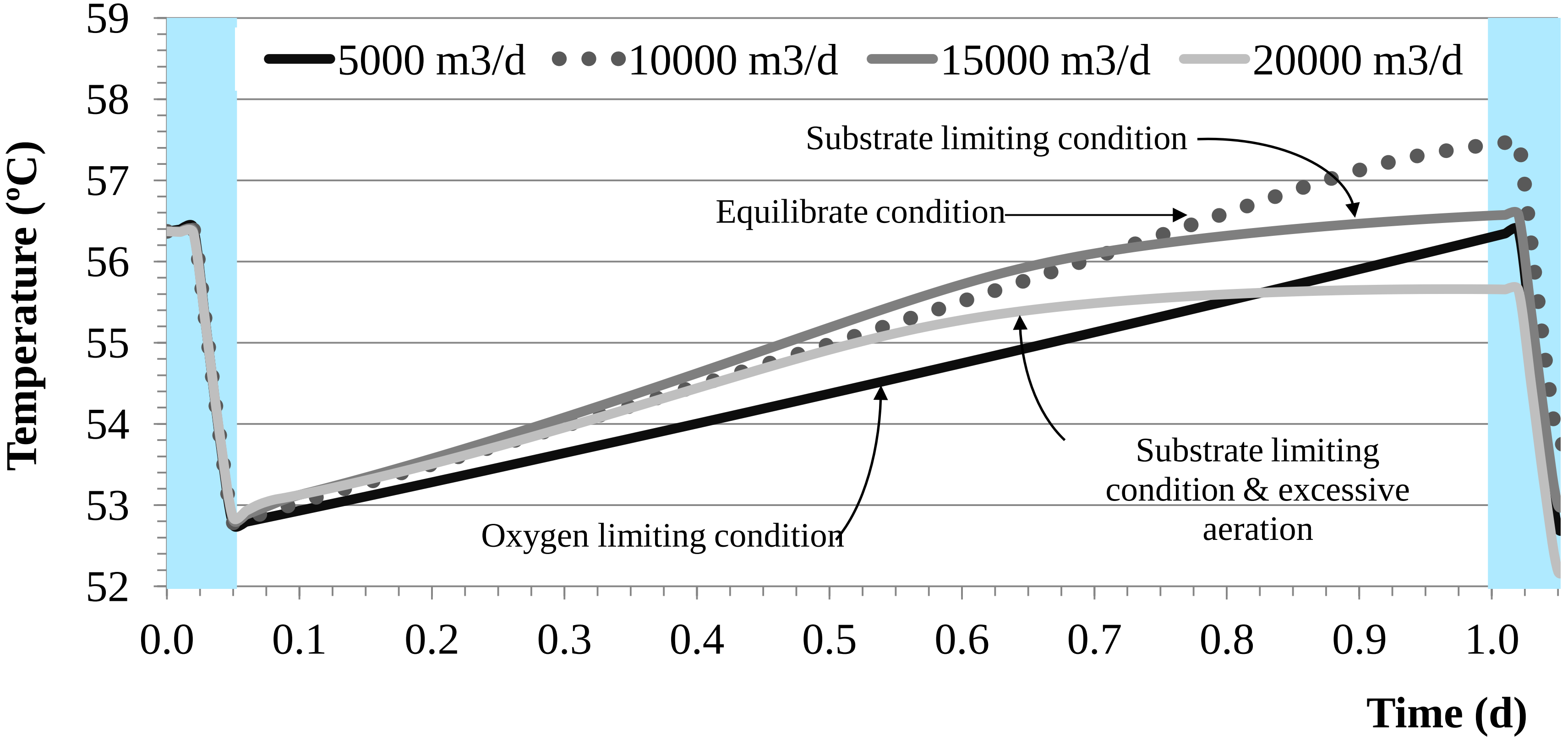

b)
1200
1000
800
600
400
200
0
-200
COD removal
Nitrification
CO2 stripping
Evaporation
Transformation heat fluxes (kW)
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Time (months)

a)

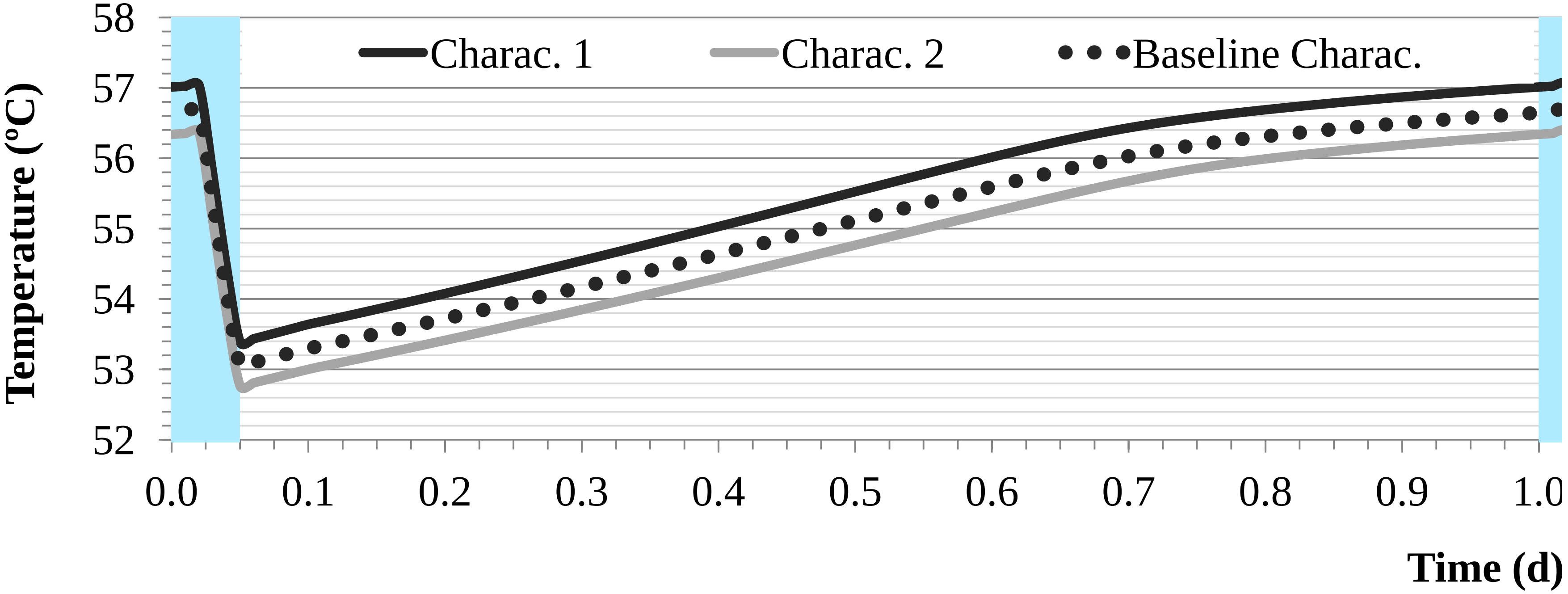


Experimental
Simulated
Temperature (ºC)
Time (d)
70
68
66
64
62
60
58
56
54
52
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

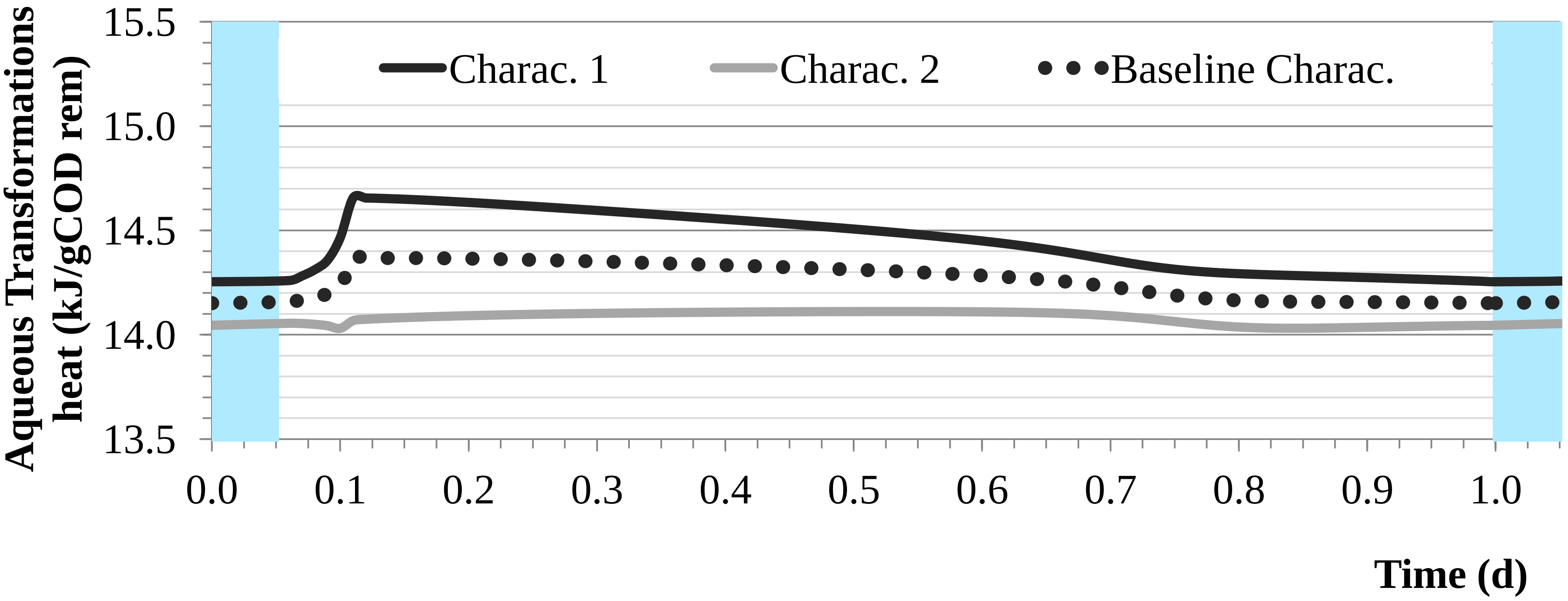

b)
ΔH mec
ΔHr water
ΔHr water-gas
ΔH cond/conv
Total enthalpy prod. & consum. (kW)
250
200
150
100
50
0
-50
-100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Time (d)


5000 m3/d
10000 m3/d
15000 m3/d
20000 m3/d
Substrate limiting condition
Equilibrate condition
Oxygen limiting condition
Substrate limiting condition & excessive aeration
Temperature (ºC)
Time (d)
59
58
57
56
55
54
53
52
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

a)


Temperature (ºC)
58
57
56
55
54
53
52
Charac. 1
Charac. 2
Baseline Charac.
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Time (d)

b)


Aqueous Transformations heat (kJ/gCOD rem)
15.5
15.0
14.5
14.0
13.5
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Time (d)
Charac. 1
Charac. 2
Baseline Charac.

- New methodology for dynamic ΔH_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