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

\( A_{\text{bubbles}} \) Contact area between aqueous phase and 2\(^{nd} \) gas phase (m\(^2\))

\( A_g \) 1\(^{st} \) gas phase surrounding area (m\(^2\))

\( A_{\text{tank}} \) Contact area between aqueous phase and 1\(^{st} \) gas phase (m\(^2\))

\( A_w \) Aqueous phase surrounding area (m\(^2\))

\( \overline{C_p}_i \) Specific heat capacity of i gaseous phase components at constant pressure (kJ g\(_E\) K\(^{-1}\))

\( C_{p_w,H_2O} \) Specific heat capacity of water at constant pressure (kJ gH\(_2O\) K\(^{-1}\))

\( \overline{E}_{ij} \) i phase stoichiometric matrix for the transformations between i and j phase

\( g \) Gravitational acceleration (m s\(^{-2}\))

\( Gr \) Grashof number

\( h_{\text{ref},i} \) Reference enthalpy of the i gaseous phase components (kJ g\(_E\))

\( h_{w,\text{ref},H_2O} \) Reference enthalpy of water (kJ gH\(_2O\))

\( H_{\text{Act}} \) Enthalpy transmitted from the actuators (kJ d\(^{-1}\))

\( H_{\text{atm_rad}} \) Longwave atmospheric radiation flux (kJ d\(^{-1}\))

\( H_{\text{Cond_Conv}} \) Surface conduction and convection enthalpy flux (kJ d\(^{-1}\))

\( H_{\text{in}} \) Input enthalpy (kJ d\(^{-1}\))

\( H_{\text{out}} \) Output enthalpy (kJ d\(^{-1}\))

\( H_{\text{sol_rad}} \) Shortwave solar radiation flux (kJ d\(^{-1}\))

\( H_T \) Net heat exchange of the analysed phase (kJ d\(^{-1}\))

\( H_{\text{trans}} \) Heat released or absorbed by the transformations in the analysed phase (kJ d\(^{-1}\))

\( k_{\text{sol_rad}} \) Total energy incident on the surface (kJ d\(^{-1}\) m\(^{-2}\))

\( k_{\text{wls}} \) Heat conduction through walls and pipes coefficient (kJ d\(^{-1}\) K\(^{-1}\) m\(^{-2}\))

\( \overline{m}_{i,\text{in}} \) Inlet i phase mass flux (gE d\(^{-1}\))

\( \overline{m}_{i,j} \) Mass flux transport between i and j phases (gE d\(^{-1}\))

\( \overline{m}_{i,\text{out}} \) Outlet i phase mass flux (gE d\(^{-1}\))

\( \overline{M}_i \) Mass vector for the components present in the i phase (gE)
\( \eta_{\text{phs,i}} \) Constant exponent of the Pr and Gr numbers (aqueous and gaseous phases conduction/convection)

NC No. of components in the \( i \) phase

NT No. of transformations in the \( i \) phase

\( P_{\text{en}} \) Power supplied by the engines and aeration systems (kJ d\(^{-1}\))

Pr Prandtl number

\( T_{\text{atm}} \) Atmospheric temperature (K)

\( T_{i} \) Phase temperature (K)

\( T_{i,\text{in}} \) Phase inflow temperature (K)

\( T_{i,\text{ref}} \) Temperature corresponding to the reference enthalpy of the gaseous phase components (K)

\( T_{w,\text{ref},\text{H2O}} \) Temperature corresponding to the reference enthalpy of water (K)

\( X_{i} \) Mass fraction of the gaseous phase components (gE \( g_{\text{E,i}} \) phase\(^{-1} \))

**Greek Symbols**

\( \alpha_{\text{phs,i}} \) Correction factor for surfaces facing up (aqueous and gaseous phases conduction/convection)

\( \alpha_{\text{rad}} \) Solar absorptivity

\( \beta_{\text{air}} \) Atmospheric radiation factor

\( \beta_{\text{phs}} \) Coefficient of volume expansion (K\(^{-1}\))

\( \delta \) Characteristic length (m)

\( \Delta h_{f} \) Specific formation enthalpy (kJ gE\(^{-1}\))

\( \Delta h_{r} \) Specific reaction enthalpy (kJ gE\(^{-1}\))

\( \Delta H_{r} \) Net reaction enthalpy (kJ d\(^{-1}\))

\( \varepsilon_{\text{atm}} \) Surface emissivity

\( \eta_{\text{en}} \) Efficiency of engines/aeration systems

\( \bar{\lambda}_{i} \) Thermal conductivity of the gaseous phase components (kJ d\(^{-1}\) K\(^{-1}\) m\(^{-1}\))

\( \lambda_{\text{atm1}} \) Surface reflectivity

\( \mu_{g_{1}} \) Dynamic viscosity of the gaseous phase components (kgE m\(^{-1}\) s\(^{-1}\))

\( \nu_{i,j} \) Rate coefficient for component \( i \) on process \( j \) (gE \( g_{\text{E,i}} \) reference component\(^{-1} \))

\( \bar{p}_{i,j} \) Kinetic rate for the transformations between \( i \) and \( j \) phases (gE \( g_{\text{E,removed component}} \) d\(^{-1}\))

\( \sigma \) Stefan Boltzmann constant (kJ d\(^{-1}\) m\(^{-2}\) K\(^{-4}\))

\( \nu_{g_{1}} \) Kinematic viscosity of the gaseous phase components (m\(^{2}\) s\(^{-1}\))

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

Subscripts

g gaseous phase

g₁ 1ˢᵗ gaseous phase

g₂ 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 \( \hat{E} \cdot \hat{p} \). 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 \(\langle \mathbf{E}, \bar{p} \rangle\) 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 \(\langle \mathbf{E}, \bar{p} \rangle\) 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.
\[
\frac{d M_i}{dt} = \sum_{j=1}^{\text{No. adj. phase}} \mathbf{E}_{i,j}^T \bar{p}_{ij} + \sum_{m} \bar{m}_{\text{phase} \rightarrow \text{out}} - \sum_{n} \bar{m}_{\text{phase} \rightarrow \text{in}}
\]
(1)
\[
i = 1, 2 \ldots \text{No. phases (number of phases)}
\]
\[
j = 1, 2\ldots \text{No. adj. phase (number of adjacent phases to phase } i)\]
Thus, the mass balance in each phase will be constructed as follows: the matrix \(\langle \mathbf{E}_{ij}, \bar{p}_{ij} \rangle\) with the
transformations that take place in the phase, plus the matrix with the transformations between
different phases \(\langle \mathbf{E}_{ij}, \bar{p}_{ij} \rangle\), 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 ($\Delta h^\circ_r$ 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).

$$\Delta h^\circ_r = \sum v_{\text{products}} \Delta h^\circ_f (\text{products}) - \sum v_{\text{reactants}} \Delta h^\circ_f (\text{reactants})$$ (2)

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

$$\Delta H^\circ_r = \sum v_{\text{products}} \rho \Delta h^\circ_f (\text{products}) - \sum v_{\text{reactants}} \rho \Delta h^\circ_f (\text{reactants})$$ (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 \textit{et al}, 2000) and the enthalpy of formation vector ($\Delta h^\circ_r$).

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

$$\Delta H^\circ_r = (\Delta h^\circ_r)^T \dot{x}$$ (5)

where,
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$_3^-$→NO$_2^-$→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 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.

\[
\frac{d M_w}{dt} = E_{w,w}^{T} \rho_{w,w} + E_{w,g1}^{T} \rho_{w,g1} + E_{w,g2}^{T} \rho_{w,g2} + \bar{m}_{w,in} - \bar{m}_{w,out}
\]  

\[
\frac{d M_{g1}}{dt} = E_{g1,w}^{T} \rho_{g1,w} + \bar{m}_{g2,g1} - \bar{m}_{g,1}
\]  

\[
\frac{d M_{g2}}{dt} = E_{g2,w}^{T} \rho_{g2,w} + \bar{m}_{g,in} - \bar{m}_{g2,g1}
\]

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 \( E_{w,w}^{T} \rho_{w,w} \) 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 \( E_{i,j}^{T} \rho_{i,j} \) 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 ($H_{\text{trans}}$), conduction and convection fluxes ($H_{\text{Cond/Conv.}}$), heat energy fluxes transmitted by the actuators ($H_{\text{Act.}}$) and short-wave (solar) and long-wave (atmospheric) radiations ($H_{\text{sol_rad.}}, H_{\text{atm_rad.}}$), as can be shown in equation 9.

\[
\frac{dH}{dt}_{\text{phase}} = \sum H_{\text{trans}} + \sum H_{\text{Cond/Conv.}} + \sum H_{\text{Act.}} + \sum H_{\text{sol_rad.}} + \sum H_{\text{atm_rad.}} + \sum H_{\text{in}} + \sum H_{\text{out}} \quad (9)
\]

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:

\[
\frac{dH_w}{dt} = - (\Delta h_{fw})^T (\bar{E}_{w,w} \bar{p}_{w,w}) - (\Delta h_{fw})^T (\bar{E}_{w,g1} \bar{p}_{w,g1}) - (\Delta h_{fg1})^T (\bar{E}_{g1,w} \bar{p}_{g1,w}) - (\Delta h_{fw})^T (\bar{E}_{w,g2} \bar{p}_{w,g2}) - (\Delta h_{fg2})^T (\bar{E}_{g2,w} \bar{p}_{g2,w}) + H_{w,g1} + H_{w,g2} + H_{w,in} - H_{w,out} \quad (10)
\]

\[
\frac{dH_{g1}}{dt} = \sum_{i=1}^{m} (\bar{H}_{g1,g2}) + \sum_{i=1}^{m} (\bar{H}_{g1,w}) - \sum_{i=1}^{m} (\bar{H}_{g,out}) + H_{phs1} - H_{g_{c,out}} - H_{atm,rad,g} + H_{sol,rad,g} \quad (11)
\]

\[
\frac{dH_{g2}}{dt} = \sum_{i=1}^{z} (\bar{H}_{g1,in}) + \sum_{i=1}^{z} (\bar{H}_{g2,w}) + \sum_{i=1}^{z} (\bar{H}_{g2,g1}) + H_{phs2} \quad (12)
\]

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 $((\Delta h_{fw})^T (\bar{E}_{w,w} \bar{p}_{w,w}))$ 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 $((\Delta h_{fw})^T (\bar{E}_{w,g1} \bar{p}_{w,g1}))$ provides the stoichiometric enthalpies of formation of the components present in the aqueous phase, and the third term $((\Delta h_{fg1})^T (\bar{E}_{g1,w} \bar{p}_{g1,w}))$ 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 ($\Delta H_r$)

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 \textit{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 CO₂ 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 m³. 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 ($k_L$), 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 ($\Delta H_r$ 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 ($\Delta H_r$ 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·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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Table 1 - Gas phase formation enthalpies

<table>
<thead>
<tr>
<th>i</th>
<th>Name</th>
<th>Formula</th>
<th>Description</th>
<th>$\Delta h^\circ_f \text{(kJ mol}^{-1}\text{)}$</th>
<th>$\Delta h^\circ_e \text{(kJ g}_{\text{stoich. unit}}^{-1}\text{)}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>$G_{\text{CO}_2}$</td>
<td>$\text{CO}_2$</td>
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<td>-32.79</td>
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<td>2</td>
<td>$G_{\text{H}_2}$</td>
<td>$\text{H}_2$</td>
<td>Hydrogen</td>
<td>0.00</td>
<td>0.00</td>
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<td>$G_{\text{CH}_4}$</td>
<td>$\text{CH}_4$</td>
<td>Methane</td>
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<td>-1.17</td>
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</tr>
<tr>
<td>4</td>
<td>$G_{\text{NH}_3}$</td>
<td>$\text{NH}_3$</td>
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<td>-3.28</td>
<td>Perry &amp; Green (1999)</td>
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<tr>
<td>5</td>
<td>$G_{\text{N}_2}$</td>
<td>$\text{N}_2$</td>
<td>Nitrogen</td>
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<td>0.00</td>
<td>Perry &amp; Green (1999)</td>
</tr>
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<td>6</td>
<td>$G_{\text{O}_2}$</td>
<td>$\text{O}_2$</td>
<td>Oxygen</td>
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<td>0.00</td>
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<td>7</td>
<td>$G_{\text{H}_2\text{O}}$</td>
<td>$\text{H}_2\text{O}$</td>
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<td>-13.43</td>
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</table>
Table 2 - Water phase formation enthalpies

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<th>$\Delta h_f^{\circ}$ (kJ g mol$^{-1}$)</th>
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<td>H$_2$O</td>
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<td>O$_2$</td>
<td>Dissolved Oxygen</td>
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<td>0.00 g mol$^{-1}$</td>
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<td>H$^+$</td>
<td>Protons</td>
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<td>0.00</td>
<td>0.00 g mol$^{-1}$</td>
<td>Brown et al. (1993)</td>
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<td>-230.00 g mol$^{-1}$</td>
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<td>(HPO$_4$)$^2$</td>
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<tr>
<td>(HCO$_3$)$^-$</td>
<td>Bicarbonate</td>
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<td>-57.59 g mol$^{-1}$</td>
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<td>-519.20</td>
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<td>C$_3$H$_6$O$_2$</td>
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<td>-510.80</td>
<td>-4.56 g mol$^{-1}$</td>
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<td>C$<em>6$H$</em>{12}$O$<em>{20}$NP$</em>{0.005}$</td>
<td>Soluble Inerts</td>
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<tr>
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<td>-1.94 g mol$^{-1}$</td>
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<td>Decy complex</td>
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<td>-2.54 g mol$^{-1}$</td>
<td>Prochazka et al. (1973)</td>
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<td>-2474.17</td>
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<td>Prochazka et al. (1973)</td>
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<tr>
<td>C$<em>6$H$</em>{12}$O$<em>{20}$NP$</em>{0.005}$</td>
<td>Sugar degrader bac.</td>
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<td>-2.537 g mol$^{-1}$</td>
<td>Prochazka et al. (1973)</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{12}$O$<em>{20}$NP$</em>{0.005}$</td>
<td>Amino-acid</td>
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<td>C$<em>6$H$</em>{12}$O$<em>{20}$NP$</em>{0.005}$</td>
<td>LCFA degrader bac.</td>
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<td>-2.537 g mol$^{-1}$</td>
<td>Prochazka et al. (1973)</td>
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<tr>
<td>C$<em>6$H$</em>{12}$O$<em>{20}$NP$</em>{0.005}$</td>
<td>Val/but degrader</td>
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<td>Prochazka et al. (1973)</td>
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<td>Propionate degrader</td>
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<td>C$<em>6$H$</em>{12}$O$<em>{20}$NP$</em>{0.005}$</td>
<td>Acetate degrader</td>
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<td>C$<em>6$H$</em>{12}$O$<em>{20}$NP$</em>{0.005}$</td>
<td>Hydrogen degrader</td>
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<td>Inorganic inert</td>
<td>-</td>
<td>-</td>
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Table 3 - Variables, parameters and expressions used in the energy balance of a C-CSTR

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
<th>Equations</th>
</tr>
</thead>
</table>
| $\dot{H}_{g,1,g2}$ | Enthalpy lost/gained by the 1st gaseous phase due to transformation (from/to the 2nd gaseous phase) | \[
\left[ (E_{g1,g2} T_{g1,g2}) \right] \left[ \begin{array}{c}
(C_{pg1}) \left(T_{g1,g2} - (T_{g1,ref})\right)
\end{array} \right] + \left( h_{g1,g2} \right)
\]
| $\dot{H}_{g,1,w}$ | Enthalpy lost/gained by the 1st gaseous phase due to transformation (from/to the aqueous phase) | \[
\left[ (E_{g1,w} T_{g1,w}) \right] \left[ \begin{array}{c}
(C_{pg1}) \left(T_{g1,w} - (T_{g1,ref})\right)
\end{array} \right] + \left( h_{g1,w} \right)
\]
| $\dot{H}_{g,2,g1}$ | Enthalpy lost/gained by the 2nd gaseous phase due to transformation (from/to the 1st gaseous phase) | \[
\left( E_{g2,g1} T_{g2,g1} \right) \left( C_{pg2} \left(T_{g2,g1} - (T_{g2,ref})\right) + (h_{g2,g1}) \right)
\]
| $\dot{H}_{g,2,w}$ | Enthalpy lost/gained by the 2nd gaseous phase due to transformation (from/to the aqueous phase) | \[
\left( E_{g2,w} T_{g2,w} \right) \left( C_{pg2} \left(T_{g2,w} - (T_{g2,ref})\right) + (h_{g2,w}) \right)
\]
| $\dot{H}_{w,g1}$ | Enthalpy lost/gained by the aqueous phase due to transformation (from/to the 1st gaseous phase) | \[
\left( E_{w,g1} T_{w,g1} \right) \left( C_{pw,H2O} \left( T_{w,g1} - (T_{w,ref,H2O}) + (h_{w,g1}) \right) \right)
\]
| $\dot{H}_{w,g2}$ | Enthalpy lost/gained by the aqueous phase due to transformation (from/to the 2nd gaseous phase) | \[
\left( E_{w,g2} T_{w,g2} \right) \left( C_{pw,H2O} \left( T_{w,g2} - (T_{w,ref,H2O}) + (h_{w,g2}) \right) \right)
\]
| $\dot{H}_{w,in}$ | Enthalpy associated with the aqueous influent | \[
\left(C_{pw,H2O} \left( T_{w,in} - (T_{w,ref,H2O}) + (h_{w,in}) \right) \right) \left( m_{w,in} \right) \left( H_{2O} \right)
\]
| $\dot{H}_{w,in}$ | Enthalpy associated with the gaseous influent | \[
\left(C_{pg1} \left( T_{g1,in} - (T_{g1,ref}) \right) + (h_{g1,in}) \right) \left( m_{g1,in} \right) \]
| $\dot{H}_{w,out}$ | Enthalpy associated with the aqueous effluent | \[
\left(C_{pw,H2O} \left( T_{w,out} - (T_{w,ref,H2O}) + (h_{w,out}) \right) \right) \left( m_{w,out} \right) H_{2O}
\]
| $\dot{H}_{g,in}$ | Enthalpy associated with the gaseous effluent | \[
\left(C_{pg1} \left( T_{g1,out} - (T_{g1,ref}) \right) + (h_{g1,out}) \right) \left( m_{g1,out} \right)
\]
| $\dot{H}_{phs1}$ | Enthalpy flow transfer between the water and the 1st gaseous phase | \[
\left( E_{g1,g2} T_{g1,g2} \right) \left( C_{pg1} \left(T_{g1,g2} - (T_{g1,ref})\right) + (h_{g1,g2}) \right)
\]

where,
\[
Gr = \frac{g \beta_{ab} (T_1 - T_{med}) \delta^3}{\left( \beta_{med} T_{med}^3 \right)} \left( \frac{\rho_{med} T_{med}^3}{m_{med} T_{med}^3} \right) \left( \frac{\dot{K}_{med} T_{med}^3}{m_{med} T_{med}^3} \right)
\]
\[
Pr = \frac{\dot{K}_{med} T_{med}^3}{m_{med} T_{med}^3}
\]
\[
\eta_{bubbles} \left( K_{2g} X_{g2} \right) \left( T_{w,ref,H2O} \right)
\]

$\dot{H}_{phs2}$ | Enthalpy flow transfer between the water and the 2nd gaseous phase | |
$\dot{H}_{gc,out}$ | Enthalpy lost/gained through walls and pipes by conduction (gaseous phase) | |
$\dot{H}_{wc,out}$ | Enthalpy lost/gained through walls and pipes by conduction (aqueous phase) | |
$\dot{H}_{am,rad,g}$ | Longwave atmospheric radiation flux (gaseous phase) | |
$\dot{H}_{am,rad,w}$ | Longwave atmospheric radiation flux (aqueous phase) | |
$\dot{H}_{sol,rad,g}$ | Shortwave solar radiation flux (gaseous phase) | |
$\dot{H}_{sol,rad,w}$ | Shortwave solar radiation flux (aqueous phase) | |
$\dot{H}_{an,in}$ | Enthalpy transmitted from the actuators (mechanical) | |
<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta h^\circ \text{r} ) Model</th>
<th>( \Delta h^\circ \text{r} ) Literature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Substrate (aq.) + ( x )O(_2) (g) ( \rightarrow ) yH(_2)O(l) + zCO(_2) (g) + Biomass</td>
<td>12.28 – 16.46 kJ/gCOD rem. (E)</td>
<td>Cooney et al., 1968</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.30 kJ/gCOD rem. (E)</td>
<td>McCarty, 1972</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.5 kJ/gCOD rem. (E)</td>
<td>Zanoni and Mueller, 1982</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.50 – 16.66 kJ/gCOD rem. (E)</td>
<td>Jewell, 1982</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.6 kJ/gCOD rem. (E)</td>
<td>Heinritz et al., 1990</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.1 – 13.7 kJ/gCOD rem. (E)</td>
<td>Messenger et al., 1992</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.8 kJ/gCOD rem. (E)</td>
<td>Pitt et al., 1995</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.68 kJ/gCOD rem. (E)</td>
<td>Riley and Forster, 2002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.4 kJ/gCOD rem. (E)</td>
<td>Shizas and Bagley, 2004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.9 kJ/gCOD rem. (E)</td>
<td>Gomez et al., 2007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.8 kJ/gCOD rem. (E)</td>
<td>Heidrich et al., 2011</td>
<td></td>
</tr>
<tr>
<td>2. ( C_6H_{12}O_6) (aq.) + 3O(_2) (g) ( \rightarrow ) 3H(_2)O(l) + 3CO(_2) (g) + Biomass</td>
<td>-893.1 kJ/mol SSU rem.</td>
<td>Gallert et al., 2005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-258.0 kJ/mol N rem.</td>
<td>Daverio et al., 2003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-102.0 kJ/mol N rem.</td>
<td>Daverio et al., 2003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-334.6 kJ/mol N rem.</td>
<td>Buttiglieri et al., 2010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-132.8 kJ/mol</td>
<td>Gallert et al., 2005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-12.4 kJ/mol</td>
<td>Oh et al., 2007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.2 kJ/mol</td>
<td>Oh et al., 2007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-9.8 kJ/mol</td>
<td>Oh et al., 2007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6 kJ/mol</td>
<td>Oh et al., 2010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.8 kJ/mol</td>
<td>Shiba et al., 2010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.9 kJ/mol</td>
<td>Oh et al., 2010</td>
<td></td>
</tr>
</tbody>
</table>

Theoretical (T) and Experimental Data (E)
Table 5 – Specific heat yields (or energy content) estimated for the different substrates used in the model

<table>
<thead>
<tr>
<th></th>
<th>$S_{SU}$</th>
<th>$S_{AA}$</th>
<th>$S_{EA}$</th>
<th>$S_{HVA}$</th>
<th>$S_{HBU}$</th>
<th>$S_{IPRO}$</th>
<th>$S_{HAC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation heats (kJ/gCOD$_{rem.}$)</td>
<td>-15.23</td>
<td>-14.38</td>
<td>-14.64</td>
<td>-14.11</td>
<td>-14.13</td>
<td>-14.16</td>
<td>-14.28</td>
</tr>
<tr>
<td>Time (d)</td>
<td>0.2</td>
<td>1.2</td>
<td>2.2</td>
<td>3.2</td>
<td>4.0</td>
<td>5.0</td>
<td>6.0</td>
</tr>
<tr>
<td>---------</td>
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<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>OLR (Kg COD/m³d)</td>
<td>2.95</td>
<td>3.00</td>
<td>3.03</td>
<td>3.35</td>
<td>3.81</td>
<td>3.51</td>
<td>3.53</td>
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</tbody>
</table>
Table 7 – Characterization of the influent

<table>
<thead>
<tr>
<th></th>
<th>Fraction of lipids</th>
<th>Fraction of proteins</th>
<th>Fraction of carbohydrates</th>
<th>Fraction of inert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Characterisation</td>
<td>19%</td>
<td>25%</td>
<td>19%</td>
<td>37%</td>
</tr>
<tr>
<td>Characterisation 1</td>
<td>15%</td>
<td>20%</td>
<td>28%</td>
<td>37%</td>
</tr>
<tr>
<td>Characterisation 2</td>
<td>22%</td>
<td>31%</td>
<td>10%</td>
<td>37%</td>
</tr>
</tbody>
</table>
Figure 1 - Schematic representation of the matrix restructuring

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
### Transformations in the aqueous phase

<table>
<thead>
<tr>
<th>AQUEOUS</th>
<th>GASEOUS</th>
<th>SOLID</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{M}<em>w (NC</em>{w1})$</td>
<td>$\tilde{M}<em>g (NC</em>{g1})$</td>
<td>$\tilde{M}<em>s (NC</em>{s1})$</td>
</tr>
<tr>
<td>$\tilde{E}_{w,w} (NT_w \times NC_w)$</td>
<td>$\tilde{E}_{g,g} (NT_g \times NC_g)$</td>
<td></td>
</tr>
<tr>
<td>$\tilde{E}<em>{w,g} (NT</em>{wg} \times NC_w)$</td>
<td>$\tilde{E}<em>{g,w} (NT</em>{wg} \times NC_g)$</td>
<td></td>
</tr>
<tr>
<td>$\tilde{E}<em>{w,s} (NT</em>{ws} \times NC_w)$</td>
<td>$\tilde{E}<em>{s,w} (NT</em>{ws} \times NC_s)$</td>
<td></td>
</tr>
</tbody>
</table>

### Transformations in the gas phase

- Liquid-Gas / Gas-Liquid transfers:
  - Evaporation / Condensation
  - Stripping / Absorption

### Liquid-Solid / Solid-Liquid transfers:
- Precipitation / Dissolution

### Gas-Solid / Solid-Gas transfers:
- Deposition / Sublimation
a)
b)

Transformation heat fluxes (kW)

- COD removal
- Nitrification
- CO2 stripping
- Evaporation

Time (months)

Jan     Feb     Mar   Apr     May    Jun     Jul     Aug    Sep     Oct     Nov    Dec
b)

Total enthalpy prod. & consum. (kW)

Time (d)

- $\Delta H_{\text{mec}}$
- $\Delta H_{\text{r water}}$
- $\Delta H_{\text{r water-gas}}$
- $\Delta H_{\text{cond/conv}}$

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
a)

Temperature (ºC)

Time (d)

Charac. 1
Charac. 2
Baseline Charac.
Aqueous Transformations

Heat (kJ/gCOD rem)

Charac. 1  Charac. 2  Baseline Charac.

Time (d)
- 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