

Modelling of Reactors for the Thermal Treatment of Waste and Biomass

F. Marias¹

Received: 24 March 2017 / Accepted: 4 August 2017 / Published online: 9 August 2017
© Springer Science+Business Media B.V. 2017

Abstract Modelling of reactors devoted to the thermal treatment of waste and biomass is a very complex task. It has to represent the physical and chemical phenomena occurring at different scales with a feedstock which is often neither completely known nor homogeneous. The first difficulty to overcome is associated to the description of the intrinsic reaction pathway of the pyrolysis reaction (which is at the center of the overall thermal treatment) and its associated kinetics. Indeed, a mathematical model has to be built to compute the rate of consumption of the initial and infinitesimal (but representative) material, the rate of production of the products of reaction as well as their nature. It has to be pointed out here that this first model should be respectful of atom balances during the overall operation. The second point that as to be addressed deals with heat and mass transfer that occur within the particle undergoing reaction. Indeed, as heat is provided to this particle, its temperature increases and when it becomes sufficient, chemical reaction begins (without any other requirement in the case of pyrolysis, or if co-reactant is also present in the case of gasification or combustion) leading to heat and mass production/consumption. These new products must be transported outside of the reactive particle under the effect of internal pressure gradients and diffusion. Then, when they have been released from the particle their future will depend upon their surrounding environment and more precisely upon the nature of the reactor (single particle, fixed bed, fluidized bed...) which will be relevant on the estimation of the extra heat and mass transfer. This short description illustrates the fact that

modeling reactors for thermal treatment of biomass requires to describe several phenomena. In this paper, we focus on a multiscale description of the relevant processes involved in the overall transformation. As a starting point, the intra particle scale is considered. Some insights into possible modelling concepts at this step are provided. Then, the particle scale is described. Once again, the important phenomena as well as the modeling options are discussed. Finally, the reactor scale is considered. These previous considerations are applied to the descriptions of model that have been developed in the case of refuse derived fuel grate gasification, combustion of sludge in a fluidized bed and pyrolysis of biomass in a fixed bed.

Keywords Modelling · Thermochemical · Reactors

Introduction

Because of the depletion of our fossil resources and given the awareness of people to the necessity of treating waste, thermochemical conversion of waste and biomass is expected to develop in the coming years [1]. Depending upon the nature of the process where this thermochemical transformation takes place (pyrolysis, gasification, combustion...), several unit operations can be put together to deliver energy into its final form (heat, electricity, gas, bio-oil...) [2]. The assemblage of such unit operations might be relatively simple (direct combustion of biomass to produce heat involves only a boiler) to highly complex (production of synfuel from biomass using Fischer–Tropsch synthesis involves biomass pretreatment, gasification, cleaning of the gas, conversion of gas into liquid fuel, hydro-conversion of this liquid...) [3]. Even though these processes are so different in nature, they all involve a place where biomass or waste is converted

✉ F. Marias
frederic.marias@univ-pau.fr

¹ Univ Pau & Pays Adour, Laboratoire de Thermique, Energetique Et Procedes-IPRA EA1932, Pau 64000, France

under the effect of heat. The place where this transformation occurs, the “reactor”, is at the heart of the present paper.

Depending upon the considered process, these reactors can be quite different (fixed or fluidized bed, entrained flow reactors, grate furnaces, rotary kilns...) [4]. However, they all involve a step where the solid fuel (biomass or waste) decomposes and releases by products that will be further converted into final products and heat. This first decomposition, primary pyrolysis, which is a chemical phenomenon, takes place when the local temperature has reached a certain threshold. For this value to be reached, energy must be transferred from a high temperature region of the above-mentioned reactor to this place, inside a so called “particle”, where the reaction takes place. And then the fluxes associated to this reactive step (heat and mass) require to be transferred from this particle to another place of the reactor to perpetuate the global process [5, 6]. The weight of these different phenomena (heterogeneous reaction, intra particle heat and mass transfer, extra particle heat and mass transfer, homogenous reactions) depends on the nature of the reactor, on its design, and on the conditions that prevail inside.

The goal of this paper is to give insights on the way these phenomena are coupled together inside the reactor and then to provide information on the way they might be transferred into mathematical formalism. Then, three examples will be given to illustrate how such models can be derived in three different situations (RDF grate gasification [7], sludge combustion in Fluidized bed [8] and biomass pyrolysis in a fixed bed [9]).

Phenomenon Under Consideration

As it was mentioned in the introduction, several physico-chemical phenomena are involved during the thermochemical conversion of waste and biomass. Three scales are required to fully describe and understand these relevant processes. The smallest one is located inside a particle, where the transformation of the fresh solid material is effective. This is the intra-particulate scale. The second one provides

information on the immediate vicinity of this particle. More precisely this “particulate” scale is used to characterize heat, mass and momentum transfer between the particle and its vicinity. Finally, the third considered scale is the one that characterises the interactions between the macroscopic phases (bed of solid, slurry, fluidized bed) held within the reactor and between these phases and the reactor itself. This is the reactor scale. Figure 1 gives insights on these three scales.

Intra Particle Scale

Let us consider a porous particle (of waste or biomass) under the effect of a reaction activator (heat) and a possible co reactant leading to its thermochemical transformation (pyrolysis, gasification, oxidation). Inside a pore of this particle, several phases might coexist:

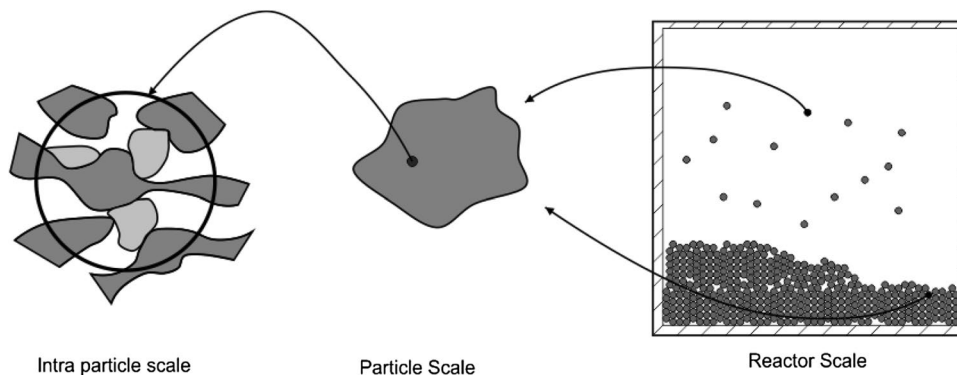
- One or more solid phases (fresh material, intermediate of transformation, residue of transformation, inorganics)
- One or more liquid phases (moisture, products of primary degradation that might condense, liquid trapped within the solid matrix)
- A gaseous and multicomponent phase (air, nitrogen, products of primary and secondary degradation).

For such a configuration, the following phenomena are involved in the thermochemical degradation:

Heterogeneous Reactions

These reactions will indeed lead to the decomposition of the fresh material into products of reaction that are often grouped into three sets (permanent gases, condensable ones and solid). Depending upon the existence of a co reactant, these reactions are pyrolysis, oxidation or gasification. These reactions will also contribute to the local temperature of the media since they might be exothermic or endothermic.

Fig. 1 Scales under consideration



Modification of the Structure of the Media

Under the effect of these reactions, solid material is converted into gas hence decreasing the local mass of solids. This reduction in the amount of the solid material leads to structural modification of the porous media, modification that can also be due to local overpressure in the gas phase (the local amount of gas increases) that might significantly break the remaining solid matrix. These structural modifications do strongly affect the local heat and mass transfer.

Phase Change

Depending upon the local temperature and pressure prevailing in the porous medium, one or more of the products of degradation might condensate and re-evaporate.

Homogeneous Reactions

These reactions involve the products of primary decomposition. They can strongly affect the local composition of the multi-component gas phase.

Transport of Liquid and Gaseous Phases

Under the effect of internal pressure and concentration gradients, migration of fluid phases inside the particle might occur. This is also the case for the individual species inside the liquid and gaseous phase.

Heat Transfer

Chemical reactions (homogeneous and/or heterogeneous) act as heat sink and sources, leading to temperature gradients within the medium. These gradients lead to heat transfer and so does the transport of liquid and gases. Radiation might also be involved in the local thermal equilibrium.

Modification of the Physical Properties

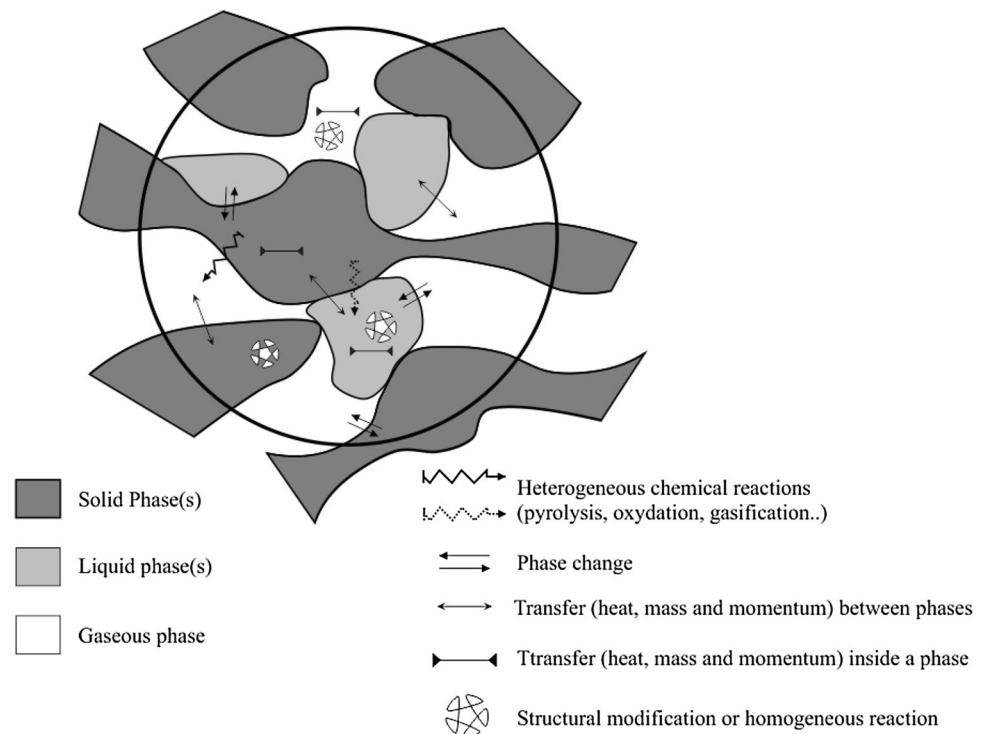
Variations in the local composition and temperature of the medium are responsible for modification of the local physical properties (thermal conductivity, heat capacity, density...). These modifications do also affect the above described phenomena.

At the intra-particulate scale, the relevant phenomena are numerous and extremely coupled. Figure 2 gives an overview of these processes.

Particle Scale

Relevant processes at this scale are mainly correlated to the direct vicinity of the particle. Several situations might occur depending upon the nature of the reactor and the mean by which the macroscopic phases are put together. Indeed, three situations (or a combination) might prevail depending upon the contact between the particle and:

Fig. 2 Processes occurring at the intra-particle scale



- The continuous fluid phase occupying the main part of the reactor (gas or liquid)
- The other particles held within the reactor
- The walls of the reactor

Given this information, the following phenomena should be considered.

Momentum Transfer

Between the fluid phase holding the particle and the particle itself. It might be associated to the transport of the particle by the fluid (fluidized bed, entrained bed, pulverulent combustion), or to the release of the products of degradation at the external surface of the particle. Collision between particles might also lead to momentum transfer as well as contact with the wall of the reactors (rotary kiln, grate furnace...).

Heat Transfer

It takes place in the immediate vicinity of the external surface of the particle. The three modes of transfer might coexist with the bulk fluid phase, with the other particles held within the reactor, and with its walls.

Mass Transfer

It occurs with the continuous fluid phase and it is either associated to the transfer from the continuous phase to the particle (case of a co-reactant for gasification) or from the particle to the continuous phase (release of the products of degradation from the particle to the continuous phase).

Heterogeneous Reactions

The direct environment of the external surface of the particle is different from the one prevailing inside the porous media. Indeed, at the external surface, there is no limitation due to intra particle mass transfer what might lead to an intensification of the reaction at this location. Moreover, if the porous media of the particle is very tight, hence decreasing

the extent of the internal mass and heat transfer to a very low value, the outer surface of the particle might be the only location where heterogeneous reactions occur.

Homogeneous Reactions

As in the case of intra particle phenomena, homogeneous reaction can occur in the vicinity of the outer surface of the particle.

Shape Modification

Because of attrition or agglomeration phenomena, particles might be split or agglomerated, hence resulting in a modification of their shape.

Figure 3 gives a representation of the phenomena that might occur at the particle scale.

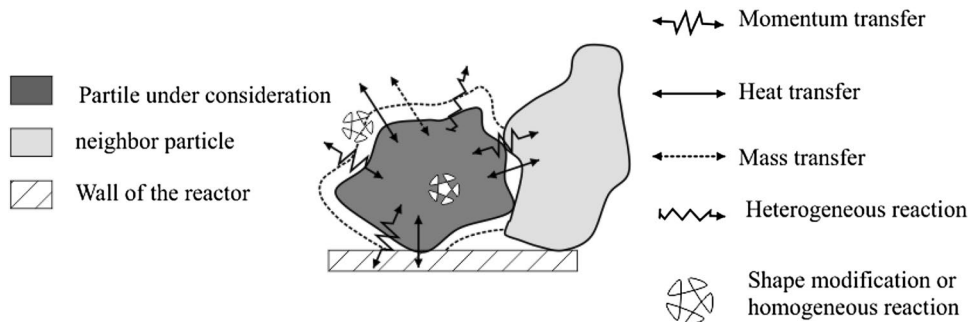
Reactor Scale

Processes that describe how the macroscopic phases are put together as well as how they flow inside the reactor are characteristics of the reactor scale. The transfer with the external environment of the reactor should be also described and discussed at this scale. These transfers concern the supply and discharge of the reactor and heat transfer by its walls. The following phenomena are relevant at this scale:

Momentum Transfer

It plays a major role in the working of the reactor. In the case of fluidized bed or slurry reactors, momentum is transferred from the continuous phase to the reactive particles of waste or biomass. This transfer ensures their motion and fixes their localization within the reactor at any time (and hence the nature of their surrounding atmosphere). In the case of reactors operating under the “bed” mode (rotary kiln, grate furnace) momentum is transferred from the wall of the reactor to the bed of particle hence conditioning its motion and mixing within the reactor. Finally, dealing with the continuous phase, this momentum transfer is of first interest since

Fig. 3 Processes occurring at the particle scale



it controls its flow and hence the direct environment of the bed (turbulence, convection...).

Heat and Mass Transfer

Mainly of the convective type, these transfers take place in the continuous phase, and in the bed of solids, but also with the walls of the reactor. Radiation is also of main concern at this scale.

Homogeneous Reactions

Reaction might occur in the continuous phase between products of primary degradation themselves or between these products and some components that might be present in the supply of the continuous phase.

Figure 4 a representation of the phenomena that might occur at the particle scale.

Modelling

As it was shown in the preceding paragraphs, processes responsible of the thermochemical transformation of waste and biomass into devoted reactors occur at three different scales. The aim of the following paragraphs is to give insight on the mathematical modelling of these phenomena.

Intra Particle Scale

At this scale, one can assume that the solid and fluid phases in contact are continuous media. It is thus possible to derive the balance equations that describe them (mass, momentum, energy), the phenomenological laws that characterize their rheological behaviour (Newton's law, Viscoelastic...) the heat and mass transfer (Fourier's Law, Radiation, Fick's law...) and the laws describing chemical reaction and equilibrium for example. Unfortunately, this kind of rigorous description is very difficult to apply since it requires the knowledge of the exact internal porous geometry, in order to integrate the preceding equations over the particle. To overcome this problem, one possible technique is to consider

a representative and elementary volume where each of the phases held within this volume can be considered as continuums and to average the equations of each phase over this entire volume rendering it homogeneous [10, 11]. Once applied, and completed with transport properties averaged over the considered volume, this method allows determining the value of the relevant properties (pressure, temperature, gaseous and solid composition) at every location inside the particle and hence to quantify the extent of the considered phenomena. This kind of work has already been used to characterize the thermal degradation of biomass for one particle [12, 13] and for a fixed bed of these particles [14]. Even though this method is very powerful and provides detailed information, it often requires high computing time, and is hence often limited to the case of a single particle.

Particle Scale

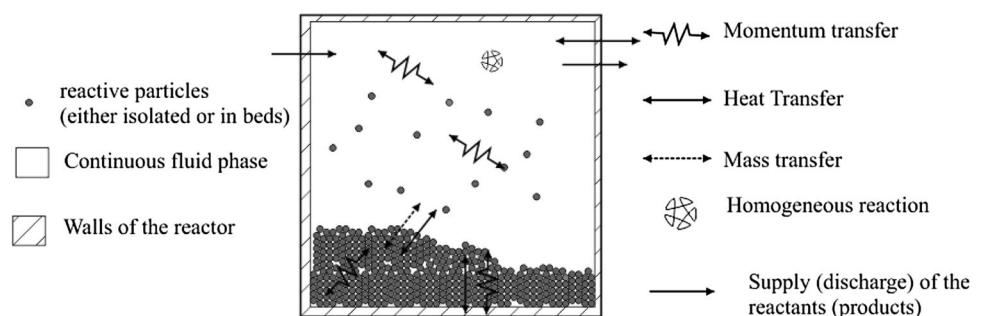
For this kind of modelling, the particle is considered as the ultimate scale. Its properties (density, temperature, composition) is then considered as uniform. The derivation of mass and energy balances over each particle, allows one computing the desired information once the chemical reaction rate (at the external surface of the particle in the case of shrinking core model or in the whole particle in pseudo-homogeneous model) has been chosen as well as the external heat and mass transfer coefficients [15]. This kind of description allows one computing the shrinking rate of the particles as well as the mass fluxes realised by each one. As it will be seen in the following sections, this method has been used to describe fluidized bed incineration of sludge or in the case of pyrolysis of aluminium based packaging [16].

Reactor Scale

Solid Phase

The possible descriptions of the solid phase are associated to its amount in the reactor. More precisely, it is often considered that when the volume occupied by the particles held within the reactor is more than 10%, the solid phase might be

Fig. 4 Processes occurring at the reactor scale



regarded as a continuum, whereas, it might be considered as an assemblage of discrete particles in the opposite case [17].

In the first case, the equations describing the particles are derived in an Eulerian reference frame. They are composed of the mass balance, the solid momentum balance [18–20], as well as the energy balance. This method allows computing the velocity field of the solid phase within any reactor geometry. It however requires that the stress tensor of the solid phase be evaluated as well as interactions between the solid and the fluid phases. This is the reason why such description is often lumped into a simplest one and the solid bed is assumed to be translated over a grate or over a rotary kiln for example [7, 16]. If the solid phase is stationary in space, but receives a batch processing, then it can be considered as an assemblage of particles or as a continuous media, using the volume averaging theory that was previously described at the intra particle scale. Such a possibility is going to be described in the next paragraph in the case of pyrolysis in a fixed bed.

When the volume fraction occupied by the solid is $<10\%$ of the reactor volume, particles might be described in a Lagrangian reference frame. A force balance including drag, gravity and other potential forces allow computing at any time the location and the velocity of every particle [21–23], given the flowfield of the fluid phase. The main goal of this method is to predict the history of the particle, in terms of temperature and composition of its surroundings, and thus its behaviour (drying, pyrolysis, heterogeneous reaction...), and finally, the location where it will release heat and mass, hence modifying the behaviour of the fluid phase. This method is strongly dependent upon the number of particles to be considered [24].

Fluid Phase

The mathematical relations that describe the fluid phase are momentum, mass, energy and species balances. A phenomenological law linking the stress tensor to the deformation rate must be added to this set, as well as a model accounting for turbulence. It is moreover necessary to provide information on the value of the transport properties (mass diffusivity, thermal conductivity, viscosity....) and on the homogeneous chemical reaction rates that might drastically influence the flow. When the geometry of the reactor is complex, the solving of the preceding equations might be quite difficult.

To overcome this situation, several possibilities exist. The first one consists in using the concept of ideal reactors [25, 26]. Using this analysis, the flow inside the reactor is perfectly defined (plug flow) or is supposed to be such that its different properties are uniform (completely stirred tank reactor). A possible approach is to use a combination of these ideal reactors. This formalism has been used in the frame of the modelling of fluidized bed combustion of

sludge, as it will be shown in the next paragraphs. Finally, when the geometry of the reactor is highly complex, and fully three dimensional, the use of CFD can be relevant [27].

Results: Case Studies

In this section, the concepts that were briefly described in the preceding paragraphs are going to be detailed for three different cases. In the first one, gasification of RDF in a grate furnace is considered, while in the second one, fluidized bed combustion of sludge is investigated. Finally, pyrolysis of biomass in a fixed bed will be considered.

Gasification of RDF

The frame of this study is collaboration between Europlasma company for the modelling of the CHO process. Very briefly, this process is composed of a grate furnace gasifier and of a high temperature reactor fed with a plasma torch to ensure thermal cracking of the tars produced in the gasifier. The gasifier under study is depicted in Fig. 5 and further information about this process can be found in [7].

The process is composed of three stages. The first one is devoted to the drying of the incoming load. It is fed with the incoming waste. The drying agent is air which is fed at the bottom of this stage. The second stage of the overall reactor is the gasifying section, it is fed at its bottom with a gasifying agent which is air. The final stage of the reactor is devoted to the decarbonation of the waste. Indeed, as

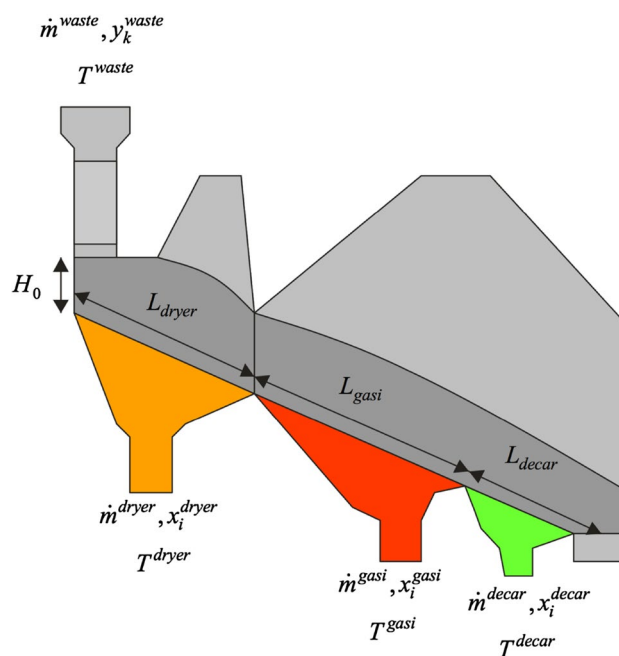


Fig. 5 Grate furnace gasifier under consideration

it will be discussed in the following sections, the waste is expected to decompose into three fractions (permanent gas, condensable gas and char) in the gasifying section. The aim of the decarbonation chamber is to convert the solid residue (char) into gas.

Information about the material that was processed and the corresponding operating parameters is provided in Tables 1 and 2.

If we focus on the two last stages, it must be noticed that the processes occurring in the solid phase (bed in motion) and in the gas phase (freeboard) are quite different but complementary. Indeed, since air is brought at the bottom of the bed, a part crosses the bed without reaction. Hence it is available at the surface of the bed to react with the products of pyrolysis which occur further downstream the bed. These reactions lead to a high temperature region (flame) that further affects the temperature of the bed. These considerations have led us to decompose the reactor into:

- A bed of solids, which is described by a one dimensional (1D) and plug flow model,
- A freeboard region, which is described by a fully three dimensional (3D) model using CFD.

Figure 6 illustrates this decomposition and the interaction between the two considered sub-models.

The complete description of the 1D model that was used can be found in [7]. It will not be detailed here. However, the main concepts and assumptions that were used are slightly discussed here. The model of the travelling bed relies on the use of the volume averaging concept [10, 11]. Once dried, the solid material is expected to decompose according to three parallel reactions into permanent gases,

Table 1 Properties of the waste and biomass used in the different models (Biomass and RDF: grate gasifier, sludge: fluidized bed combustor, maritime pine: fixed bed pyrolysis)

Waste	Mixture of biomass and RDF	Sludge	Maritime pine
Ultimate analysis (% mass, raw basis)			
Moisture	17.7	75.4	11.36
Organic	75.9	20.44	86.64
Inorganic	6.4	4.16	2.00
Proximate analysis (%mass, dry ash free)			
C	52.3	58.97	51.00
H	6.1	8.21	6.00
O	40.6	26.77	42.00
N	1.00	5.44	3.00
S	0.00	0.54	0.00
Cl	0.00	0.07	0.00
Lower heating value (MJ/kg, raw basis)			
LHV	17.43	3.8	19.36

Table 2 Operating conditions for the grate gasifier

Operating conditions	
Waste supply	
Mass flow rate (t/h)	6.25
Temperature (°C)	25.00
Mean diameter (mm)	13.05
Height of the bed of solids (m)	0.95
Drying	
Volumetric flow rate of air (Nm ³ /h)	7000.00
Temperature (°C)	360.00
Gasfying	
Volumetric flow rate of air (Nm ³ /h)	5400.00
Temperature (°C)	600.00
Decarbonation	
Volumetric flow rate of air (Nm ³ /h)	1300.00
Temperature (°C)	25.00
Equivalence ratio	
Gasyfing + decarbonation (%)	22.86

tars and char. The gas phase is supposed to be composed of 17 species (N₂, O₂, H₂, H₂O, CH₄, CO, CO₂, H₂S, SO₂, HCl, HCN, NH₃, NO, NO₂, C₁₀H₈, C₇H₈, C₆H₆), 15 of them being released during the pyrolysis step. Homogeneous reaction (in the gas held in the bed) is accounted for and heterogeneous reaction of the pyrolysis residue is also taken into account (with O₂, CO₂, and H₂O). Special attention has been given to the composition of the primary pyrolysis products and to the kinetics of the reactions so that the atom balances is ensured during this first step, and hence during the overall process. This bed model requires,

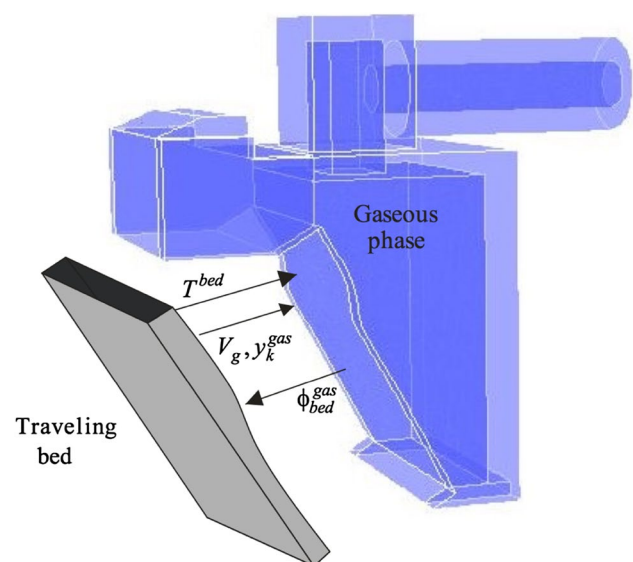


Fig. 6 Grate furnace gasifier under consideration

as a numerical input, the heat flux received from the freeboard by both convection and radiation. This allows computing all the variables of the model and thus to provide the information on the composition and velocity of the gas leaving the bed at every position over the grate. This information is used as boundary conditions for the “CFD” 3D model. Ansys software was used in this frame, using physical sub-models accounting for turbulence (k- ϵ model), homogeneous reaction (reaction rate computed according to the limiting step between kinetic and micro mixing) and radiation (discrete ordinates model).

Iterations between the two sub-models (bed model and freeboard model) are then performed until convergence is reached (no more evolution of the exchange variables between one iteration to another).

Figure 7 represents respectively the evolution of the average mass fraction of each phase in the bed, the intrinsic average mass fraction of species contained in the gas leaving the bed, and of the temperature of the bed along the reactor. On these figures the dashed vertical lines represent the limits of the drying and gasyfing sections. It can be seen that, in the drying stage, the evaporation of free water from the bed leads to a decrease of its moisture content and to an increase in the H_2O concentration in the gas phase. Also, because equilibrium is assumed between liquid and gaseous water in the bed, some vapour is present in the bed as it is supplied to the drying section. When air is blown below the grate, it brings some of this vapour to the freeboard of the bed and this is the reason why the composition of the gas leaving the bed at the entrance of the drying section is not

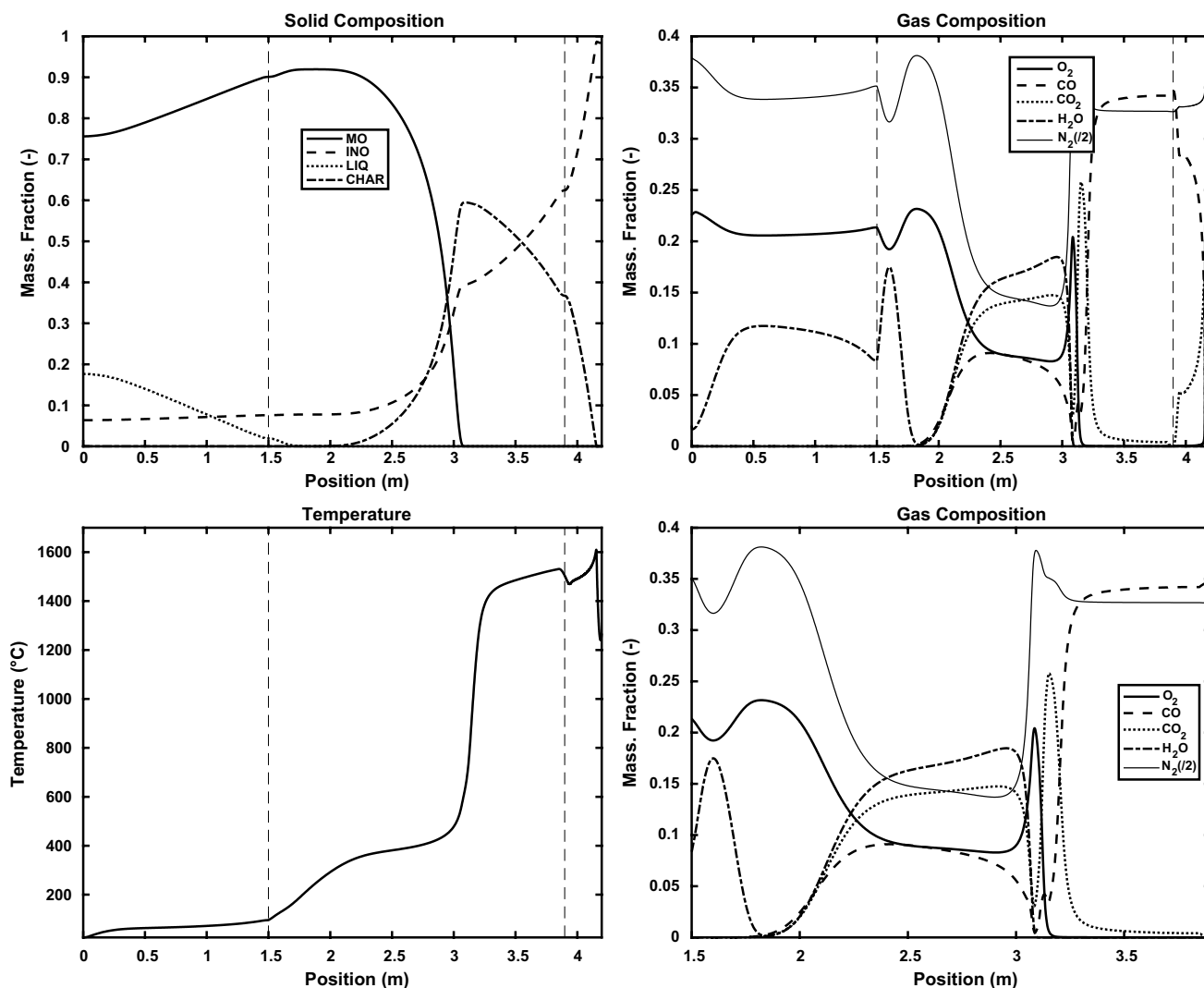


Fig. 7 Evolution of the average mass fraction of each phase in the bed along the reactor (*up-left*), evolution of the intrinsic average mass fraction of species within the gaseous phase of the bed (*up-right*), and

evolution of temperature in the bed along the reactor (*bottom-left*). Zoom on the gasifying section for gas composition (*bottom-right*)

the one of pure air. Despite the high value of the temperature of the drying agent entering the bottom of the bed (air at 360 °C), the temperature of the bed in the drying section does not increase above the wet temperature in that section, because of the presence of liquid water. As the waste enters the gasifying section, and because of the value of the temperature of the gasifying agent (600 °C), there is an increase in the evaporation rate which contributes to the rapid collapse of the liquid water content in the bed. At this position, the temperature of the bed begins to increase until the pyrolysis processes. At this position, and because it has been set as an assumption as an endothermic process (100 kJ/kg for reaction “Organic Matter → char”, 100 kJ/kg for “Organic matter → permanent gases”, 100 kJ/kg for Organic Matter → tars), the temperature reaches a threshold which is kept until the end of the process. This pyrolysis step affects the composition of the bed (decrease of the organic material and increase of the char) and the gas held in the bed because of the release of volatiles by pyrolysis. At the end of the pyrolysis, the O₂ content raises again to its value in pure air (0.23) because the air entering the furnace below the grate is no more diluted nor consumed by the release and partial oxidation of volatiles. Under the effect of radiation

from the freeboard (computed by the CFD model), the temperature of the bed starts to increase again what allows the combustion reaction of char to become significant. At this point, the temperature increases sharply and the reaction of char becomes limited by the lack of oxygen. This situation continues until the temperature of the bed is sufficient for the gasification of char by carbon dioxide to begin. Because this last process is endothermic, the temperature of the bed reaches a second threshold, and this is also the case for carbon dioxide (which is consumed by the gasification reaction) and for carbon monoxide which is produced by both oxidation and gasification reactions. As the bed of solids enters the decarbonation region, there is a slight decrease in the value of the temperature because of the low value of the temperature of the air entering the grate (25 °C). This leads to a modification of the rate of consumption of char and carbon dioxide (oxygen is still completely consumed) and this new rate is also affected by the decrease to zero of the char content. Then, once the char is completely consumed the oxygen level returns to its value in air (0.23) and the temperature of the bed decreases under the effect of the cooling by fresh air.

As a result of the CFD computation, Fig. 8 shows fields of oxygen, methane, carbon monoxide, carbon dioxide and

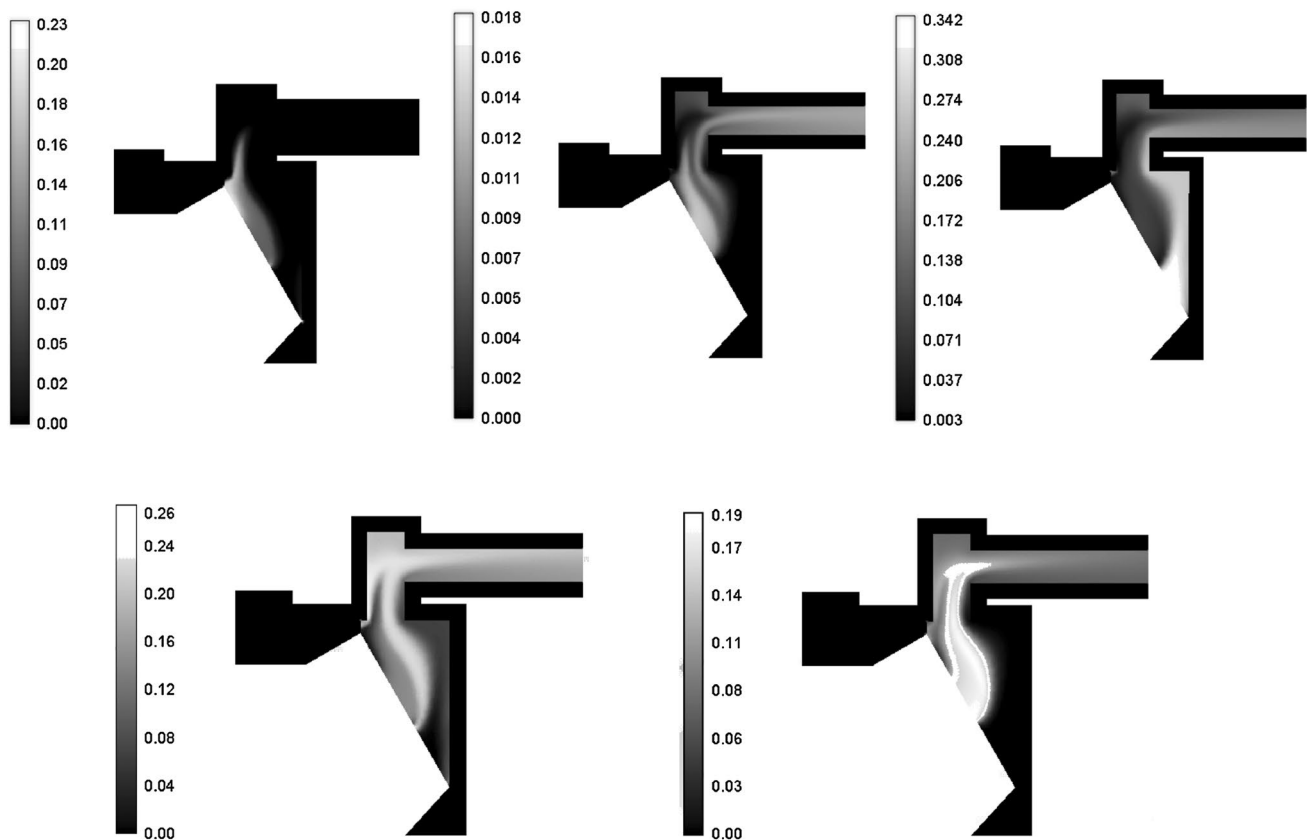


Fig. 8 Profile of mass fraction of oxygen (*up-left*) methane (*up-centre*) carbon monoxide (*up-right*), carbon dioxide (*bottom-left*) and water (*bottom right*) in the gaseous phase of the second chamber (gasification + decarbonation) of the reactor

water within the freeboard. As it can be seen, some oxygen leaves the bed unreacted and hence, it becomes available for oxidation of the volatiles released from the bed. This oxidation takes place as a sharp “flame” over the bed, which can be seen by the decrease of the methane and carbon mass fraction as these species cross this region, while carbon dioxide and water contents are increased here. It can also be said that all of the available oxygen is consumed before it leaves the second chamber of the reactor, and that the carbon monoxide produced by the gasification of char is not at all affected by this oxygen escaping unreacted from the bed. It must be noticed here that, even though the overall mass balance is fully satisfied, overall atom balances (ie., after the convergence of the coupled bed and CFD sub-models) are satisfied up to 98.34, 98.87, and 101.98% for carbon, hydrogen and oxygen respectively.

These discrepancies in the atom balances are associated to the iterative scheme of the overall convergence process and to the nature of the reactions taken into account. Indeed, to compute the extent of reaction in the bed of waste, it is required that the heat flux it receives is provided to the 1D model. At the beginning of the convergence process, the heat flux is “guessed” from other computation (initialization). Given this guess heat flux, the composition of the volatiles (of reaction organic matter → permanent gases and organic matter → tars) is computed in order to fulfil the atom balances (with less than 10^{-6} relative error). This “initial” composition of the volatiles is kept during the overall convergence process. Nevertheless, as the iteration take place, the heat flux received by the bed of solids slightly differs from the initial guess. Hence, the profile of temperature is also modified from the one computed at first iteration. As the temperature profile is modified, so is the extent of the three parallel reactions. This means that the ratios tars/permanent gases and tars/char are different from the ones at first iteration, keeping the overall mass balance satisfied (up to 10^{-6} relative error), but leading to small deviations in the atom balances.

These discrepancies could be avoided if the composition of the volatiles was computed at each overall (1D model-CFD model) iteration. Nevertheless, since the deviations in atom balances are believed to be small, we have kept the initial compositions in the present case.

Fluidized Bed Combustion of Sewage Sludge

The frame of this study is collaboration with Veolia Environnement Company. Its aim is to develop a model able to predict the influence of the operating parameters of the industrial unit (sludge flow rate, position of the injector of sludge, moisture content...) (Fig. 9) on the composition of the gas leaving the combustor. The complete description of the derivation of the model is not the scope of the present

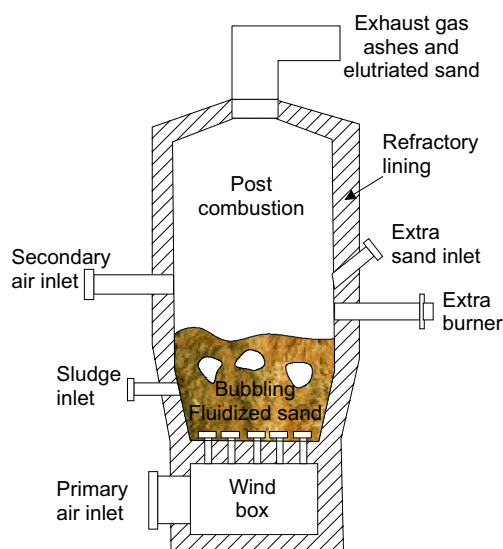


Fig. 9 Scheme of the combustor under consideration

publication. Instead, it is preferred here to describe the main concepts on which the model relies on as well as its main assumptions. Interested reader should refer to [8, 28, 29] for a precise description of the equations of this model.

Dealing with the modelling of fluidized beds, it is first required to derive a so called “hydrodynamics” model, describing the partitioning of the air introduced at the bottom of the reactor and its interaction with the sand used as a thermal buffer for the operation. The assembly of sub regions that were put together to finally build the overall model is depicted on Fig. 10.

Basically, the gas phase is supposed to be distributed over five regions (bubble, buffer, emulsion, disengagement, and post combustion). Each of these regions has its own properties and characteristics (Plug flow for gas in the bubble, disengagement and post combustion zones, CSTR for gas in the emulsion zone, and 2D for gas held in the vicinity of the bubbles). The sand is distributed over the disengagement, the buffer zone and the emulsion which ensures quasi thermal homogeneity of the temperature prevailing in these zones. The sludge particles (which might be fed to the reactor in the bed or in the freeboard) are transported in the dense bed according to a “diffusion like” law, why they are transported by convection in the freeboard (fall or elutriation). They are assumed to be spherical, undergoing:

- Drying (driven by water vapor concentration difference between the surface of the particle and the gas phase in the surroundings),
- Kinetically controlled pyrolysis (which is supposed to be a single step reaction ensuring atom conservation),

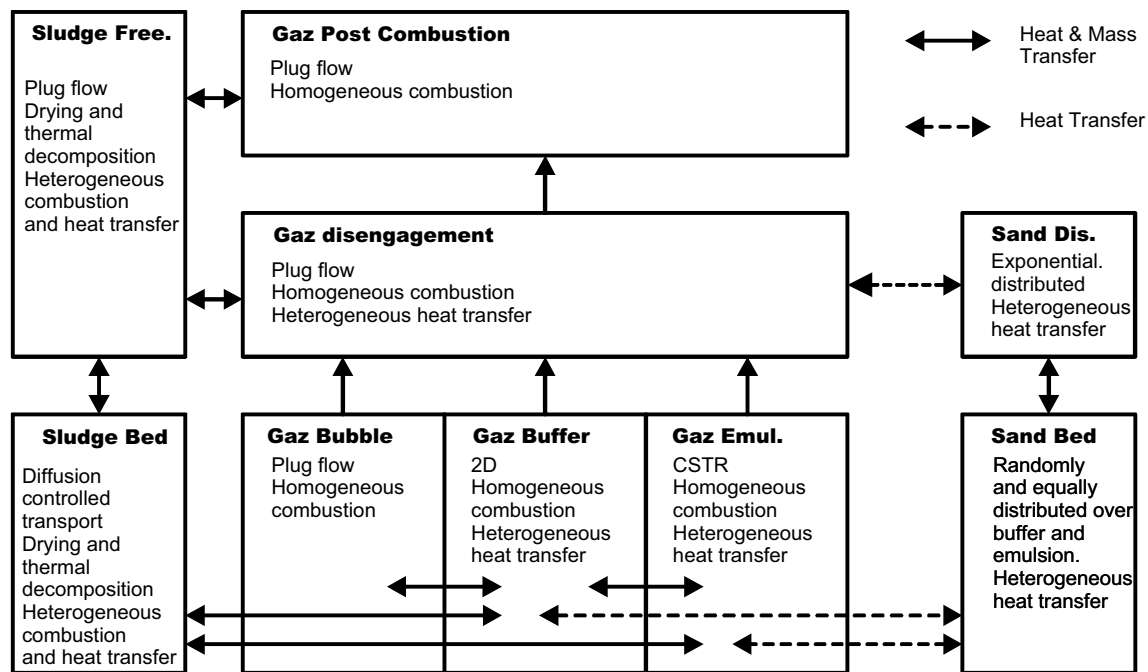


Fig. 10 Complete description of the different zones of the fluidized bed model and of their connections

- Char combustion using a shrinking core model where the external rate of reaction might be limited by kinetics or mass transfer of oxygen at the surface of the particle.

The gases released during these steps are further converted into the different gaseous regions, according to the kinetics of hydrocarbons combustion and water gas shift reactions. Special attention has been paid to the treatment of nitrogen. A part of it is expected to be released as volatiles during pyrolysis while the remaining part is expected to stay in the solid matrix with the pyrolysis residue. This part is then released when char is consumed by combustion. The model developed by Liu and Gibbs [30] was also included to ensure estimation of the N_2O formation and consumption. Hence, the final “ NO_x ” model includes:

- Thermal NO
- Release of a part of fuel_N into HCN and NH_3
- Remaining of a part of fuel_N into the pyrolysis residue
- Homogeneous transformation of HCN and NH_3 into N_2 , N_2O and NO
- Heterogeneous transformation of char bound nitrogen into N_2 , N_2O and NO.

The results that might be obtained by this model range from fields of temperature and composition at every location of the reactor, to evolution of the composition of the gas as functions of the operating parameters. Thanks to an experimental campaign that was performed on an industrial unit

during a week on a site owned by Veolia group; it was possible to compare the numerical predictions of the model at the output of the reactor to measurements that were performed on the pipe leaving the industrial reactor once steady state was reached using a gas analyser. Such Figures are presented on Figs. 11 and 12. The operating conditions corresponding to the different runs that are referred to on the figures are given in Table 3 while the main characteristics of the sludge being incinerated are provided in Table 1.

Regarding Fig. 11, it can be said that the model perfectly fits the measured values for oxygen and hydrogen chloride for every run. Indeed, whether the sludge flow rate is modified or the extra gas fed to the reactor, the model correctly predicts the composition of the gas (this is also the case for carbon dioxide and carbon monoxide even though these values are not presented here). Dealing with the nitrogen emissions (in the form of NO or N_2O , Fig. 12), the model also show a very good ability to reproduce the experimental measurements. There are however two runs ($n^{\circ}4$ and 5) for which the model fails to correctly estimate the distribution of the nitrogen in the flue gas. Indeed, the model under predicts the N_2O production while it over predicts the NO one. Several issues in the modelling effort might explain this discrepancy. Indeed, as it has been showed by Skreiberg et al. [31] and Alex and Castaldi [32] the main issue in the NO_x overall transformation is associated to the homogenous reactions of HCN and NH_3 released by pyrolysis of the incoming material (sludge in our case). In our modelling effort, this transformation is taken into account through eight homogeneous

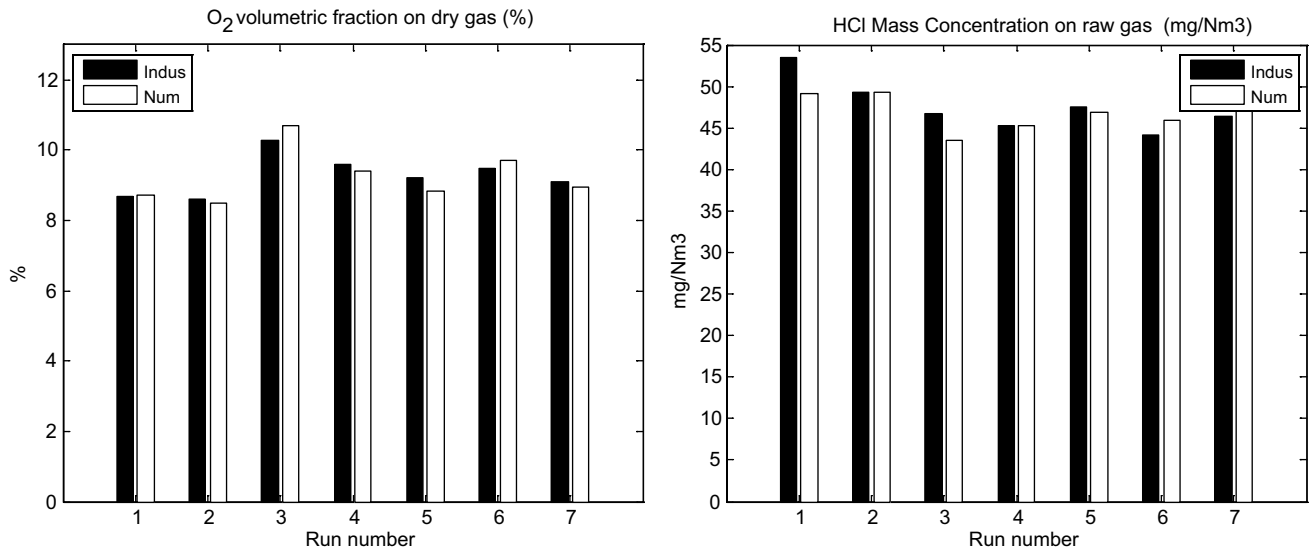


Fig. 11 Value of the composition of the gas (main compounds) during the test runs. (Industrial at air flume before the flue gas treatment unit, Numerical at the outlet of the equivalent reactor)

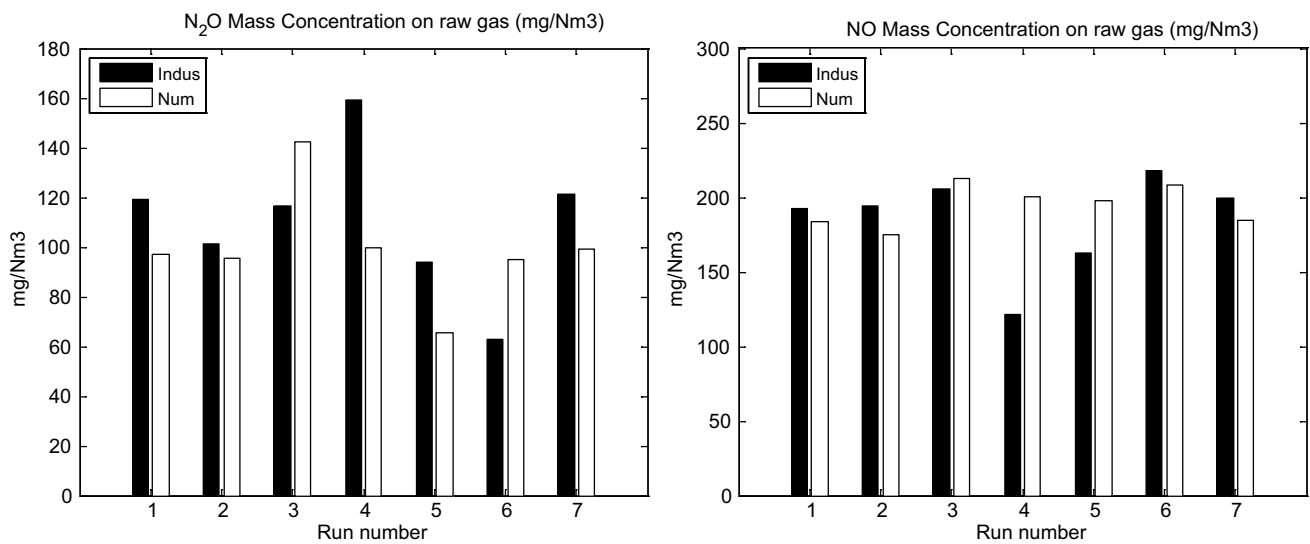


Fig. 12 Value of the N₂O and NO concentration of the gas during the test runs. (Industrial at air flume before the flue gas treatment unit and with the SNCR unit switched off, numerical at the outlet of the equivalent reactor)

Table 3 Operating conditions for the fluidized bed incineration of sludge

Run n°	1	2	3	4	5	6	7
Sludge flow rate (t/h)	2.38	2.41	1.82	2.11	2.24	2.20	2.18
Flow rate of freeboard extra gas (Nm ³ /h)	0.26	0.52	0.13	0.45	0.91	0.15	0.68
Flow rate of dense bed extra gas (Nm ³ /h)	0.00	1.27	0.00	5.27	5.67	1.40	2.45
Flow rate of primary air (Nm ³ /h)	5334	5207	4932	5260	5301	5298	5034
Flow rate of secondary air (Nm ³ /h)	54.9	231.0	0.0	97.5	156.0	256.0	134.0
Temperature of primary air (°C)	517	540	503	418	519	532	534
Average temperature of the bed (°C)	707	705	734	702	738	764	705

reactions and two heterogeneous reactions (and associated kinetics) involving oxidation and reduction. One possible source of discrepancy is also the ratio of fuel nitrogen remaining in the solid after pyrolysis. In our case, this ratio has been fixed in order to keep the molar ratio C/N constant during pyrolysis. Finally, the heterogeneous reaction of char (containing nitrogen) and associated kinetics might also lead to discrepancies in the numerical prediction. Nevertheless, regarding Fig. 12, there is some evidence that the model reproduces quite well the measured values at industrial scale on most of the runs. Hence, we assume that the observed discrepancies could also be associated by uncertainties on the exact values of the operational parameters or on the fact that complete steady state operation might not be reached during the industrial runs under consideration.

This set of results have led us to think that the model was validated and hence that it can be used to get a better understanding of the transformation of the sludge in the reactor. Such a possibility could be done by analysing the internal profiles of species inside the reactor as they are presented on Fig. 13 which was obtained in the case of Run n°2 (Table 3). On the left part of the figure, one can observe the profile of temperature in the different zones of the model. Even though its value is quite homogeneous within the reactor, one can notice that the emulsion zone (where drying and pyrolysis occur) is colder (around 160 °C less) than the bubble or the freeboard zones. The highest temperature is encountered in the disengagement zone (just above the bed) where the main part of the oxygen entering the fluidized bed as bubbles is

finally mixed with the volatiles (released by pyrolysis in the emulsion zone) as the bubbles burst at the top of the dense bed. For the main species held in the gas, their concentration is only slightly modified once this disengagement zone has been crossed. However, the transformation of nitrogen is strongly affected by the temperature profile and its transformation takes place all over the reactor.

Pyrolysis in a Fixed Bed

The last application that is going to be described here deals with the modelling of pyrolysis in a fixed bed. More particularly, this model has been built to represent batch pyrolysis in a high capacity thermobalance. This device [33] is quite similar to commercial TGA, but, it can accept a load of biomass or waste of up to 1 kg, depending upon the density of the material. The device under consideration is depicted on Fig. 14. Basically, a basket holds a load of organic material for which information on its thermal degradation is desired. Due to the electrical furnace in which the basket is located, and thanks to a nitrogen supply, pyrolysis conditions can be reached and recorded, as well as the mass of the sample during the experiment.

Once again, the scope of the present paper is not to provide the information regarding the derivation of the model. Further information regarding the model itself should be found in [9]. In this case, in order to describe the transfers (heat and mass) as well as the reactions occurring with the sample being processed, the volume averaging theory has

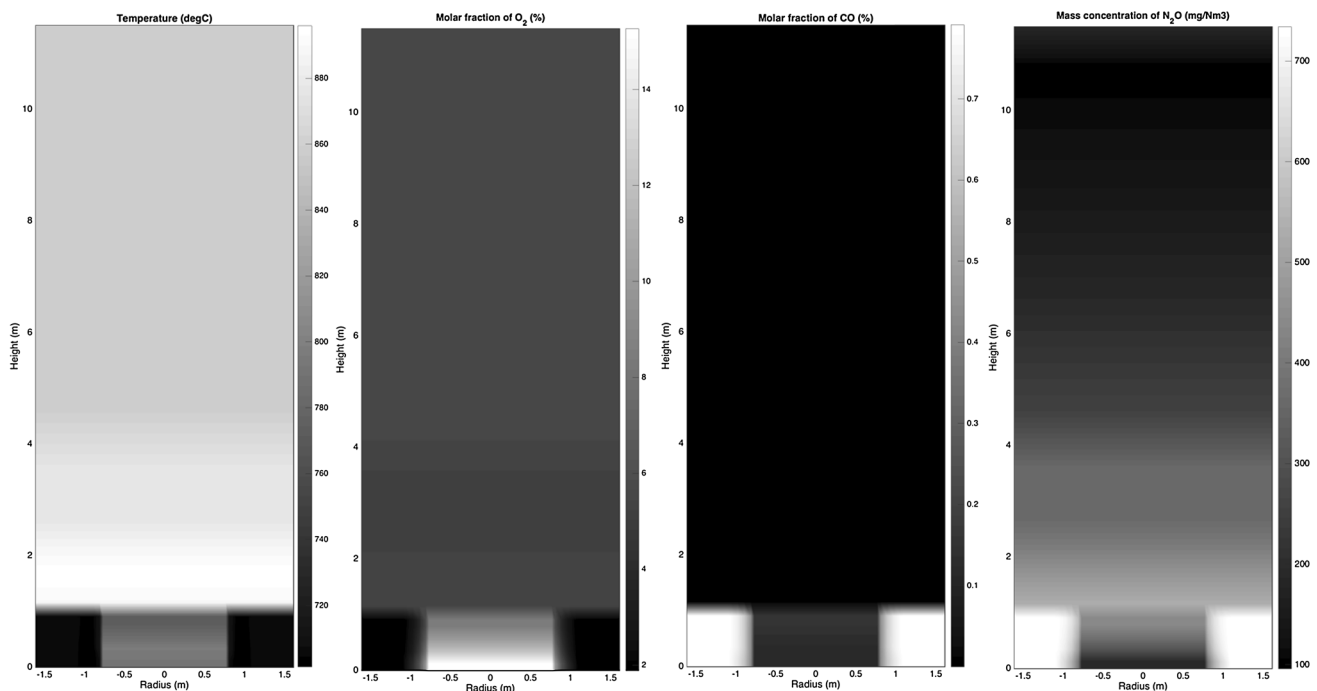


Fig. 13 Fields of temperature, oxygen, carbon dioxide and nitrous oxide computed in the model

Fig. 14 High capacity thermobalance at LaTEP (*left front view, right side view*)



been used [10, 11]. More precisely, four solid phases were taken into account (fresh material, intermediate, char, inorganic material), one liquid phase (pure water representing moisture content), and one multicomponent gaseous phase (composed of 16 species). Derivation of the classical balance equations over each of the phase where then integrated and averaged over an elementary and representative volume. Pyrolysis of fresh material was accounted for using a two successive and three parallel reactions scheme.

A batch of 250 g of maritime pine (Table 1) shredded with an average diameter of 1 mm was processed in the experimental device. During the first 6 min of the experiment, pure nitrogen is supplied to the furnace so that it becomes oxygen free. Then the temperature is raised to 110 °C at 10 °C/min and kept at this value during 60 min for the drying of the sample to take place. After this step, the temperature is raised to 285 °C at 20 °C/min and this temperature is kept for 5 min. The sample is then cooled at a rate linked to the thermal losses of the furnace (no more heat is provided to the system). The mass loss of the sample is presented on Fig. 15. One can see that drying of the sample is completed before the end of the drying step (the mass loss is 11.36% and the mass of the sample is stable) and then, as the temperature is further increased, the organic material is decomposed under the effect of heat and at the end of the experiment, the total mass loss is 36.5%. This experimental mass loss is compared to the one predicted by the model. As one can see, the model fits quite well the experimental values, what shows that it is able to represent both the heat and mass transfers as well as the reaction. We estimate that this comparison provides a certain degree of validation to our model and this is the

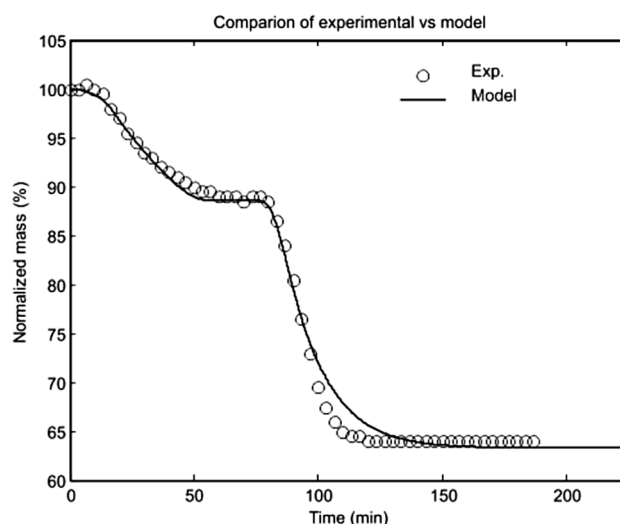


Fig. 15 Transient evolution of the mass of the sample numerical versus experimental

reason why we feel confident in using it for an in-depth analysis of the process. Such an analysis can be performed in terms of internal profiles of fresh organic matter inside the basket (Fig. 16). The nine profiles represented on the figure represent the transient evolution (in terms of percentage of the initial organic content) of the organic material in the transverse plane of the basket. The nitrogen (heated by the furnace) enters the basket by its bottom. Before the end of drying ($t \leq 75$ mn, the temperature of the sample is not enough for the pyrolysis reaction to take place). Then at $t = 82$ mn, because the temperature of the furnace starts to increase again, pyrolysis begins. As one

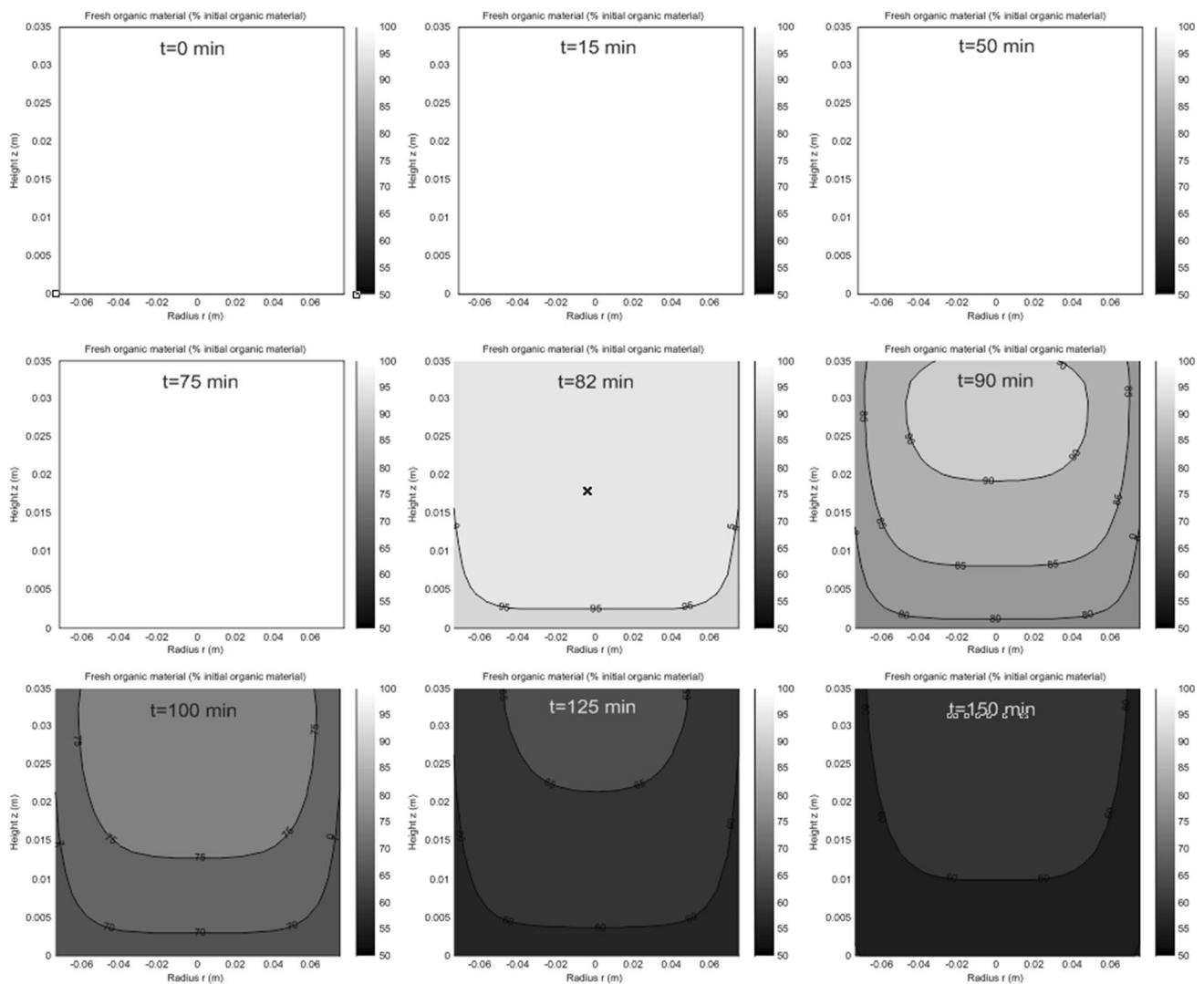


Fig. 16 Numerical profiles of mass concentration of “fresh” organic material within the sample

can see, its progression is not uniform within the sample. Indeed, because the boundary conditions are different on the sides (no mass transfer, heat conduction with the metal of the basket), on the bottom (supply of hot nitrogen), and on the top (exhaust of the mixtures of volatiles and nitrogen) of the sample, the pyrolysis is mainly controlled by the heat transfer within the sample, which is itself affected by the endothermic pyrolysis. Indeed, even though there is some uncertainty about the endothermic or exothermic nature of pyrolysis (see for example the work of Ciuta et al. [34]. and Turner et al. [35]), it has been assumed in our work that the process was endothermic. Given this information, one can see that the pyrolysis progresses from the bottom and the sides of the sample towards a core which is located on the upper center part of the process. One can also see that at the end, the extent of reaction is almost the same everywhere in the sample.

Conclusion

This article has given insights on the modelling of reactors devoted to thermochemical transformation of waste and biomass. In the first section, the different phenomena that could occur in such systems have been summed up and described. Then in the second step, some elements have been proposed to consider the different modelling strategies that might exist. It must be emphasized here that the elaboration of a mathematical model should always be related to the information that is wanted and that, too much complexity could make the solving difficult, and hence preventing the mathematical model to be helpful. Finally, in the third section, some examples of models that have been developed at LaTEP for specific cases have been presented as well as the nature of the results these models can provide.

References

1. Scarlat, N., Dallemand, J.F., Monforti-Ferrario, F., Nita, V., Peng, J., Bi, X.T.: The role of biomass and bioenergy in a future bioeconomy: policies and Facts. *Environ. Develop.* **15**, 3–34 (2015)
2. Demibas, A.: *Biofuels, Securing the Planet's Future Energy Needs*. Springer, London (2009)
3. Kamm, B., Gruber, R., Kamm, M.: *Biorefineries-Industrial Processes and Products: Status Quo and Future Directions*. Wiley, Weinheim (2008)
4. Dufour, A.: *Thermochemical Conversion of Biomass for the production of Energy and Chemicals*. Wiley, Weinheim (2016)
5. Balat, M.: Mechanisms of thermochemical biomass conversion processes. Part 1: reactions of pyrolysis. *Energy Sources Part A* **30**, 620–635 (2008)
6. Demirbas, A., Arin, G.: An overview of biomass pyrolysis. *Energy Sources* **24**, 471–482 (2002)
7. Bernada, P., Marias, F., Deydier, A., Couture, F., Fourcault, A.: Modeling of a traveling bed waste gasifier. *Waste Biomass Valor.* **3**, 333–353 (2012)
8. Marias, F., Benzaoui, A., Vaxelaire, J., Gelix, F., Nicol, F.: Fate of nitrogen during fluidized incineration of sewage sludge. Estimation of NO and N₂O content in the exhaust gas. *Energy Fuels* **29**, 4534–4548 (2015)
9. Marias, F., Delage, S.: Modeling of pyrolysis in a high capacity thermobalance. *Can. J. Chem. Eng.* **93**, 261–275 (2015)
10. Whitaker, S.: *The Method of VOLUME Averaging*. Springer, Dordrecht (1999)
11. Pommier, S., Chenu, D., Quintard, M., Lefebvre, X.: Modelling of moisture-dependent aerobic degradation of solid waste. *Waste Manag.* **28**, 1188–1200 (2008)
12. Ratte, J., Marias, F., Vaxelaire, J., Bernada, P.: Mathematical modelling of slow pyrolysis of treated wood waste. *J. Hazard. Mater.* **170**, 1023–1040 (2009)
13. Gronli, M.: A theoretical and experimental study of the thermal degradation of biomass. PhD Thesis, The Norwegian University of Science and Technology (1996)
14. Ratte, J., Fardet, E., Mateos, D., Hery, J.S.: Mathematical modelling of a continuous biomass torrefaction reactor: TORSPYD™ column. *Biomass Bioenergy* **35**, 3481–3405 (2011)
15. Doraiswamy, L.K., Sharma, M.M.: *Heterogeneous Reactions: Analysis, Examples, and Reactor Design*. Volume 1: Gas–Solid and Solid–Solid Reactions. Wiley, Hoboken (1984)
16. Marias, F., Roustan, D., Pichat, A.: Modelling of a rotary kiln for the pyrolysis of aluminium waste. *Chem. Eng. Sci.* **60**, 4609–4622 (2005)
17. Crowe, C., Sommerfield, M., Tsuji, Y.: *Multiphase Flows with Droplets and Particles*, CRC Press, Boca Raton (1998)
18. Ding, J., Gidaspow, D.: A Bubbling fluidization model using kinetic theory of granular flow. *AIChE J.* **36**, 523–538 (1990)
19. Pape, R., Gidaspow, D.: Numerical simulation of intense reaction propagation in multiphase systems. *AIChE J.* **44**, 294–309 (1998)
20. Yang, Y.B., Goh, Y.R., Zakaria, R., Nasserzadeh, V., Swithenbank, J.: Mathematical modelling of MSW incineration on a travelling bed. *Waste Manage.* **22**, 369–380 (2002)
21. Patankar, N.A., Joseph, D.D.: Modeling and numerical simulation of particulate flows by the Eulerian–Lagrangian approach. *Int. J. Multiph. Flow* **27**, 1659–1684 (2001)
22. Zhou, H., Flamant, G., Gauthier, G., Lu, J.: Lagrangian approach for simulating the gas-particle flow structure in a circulating fluidized bed riser. *Int. J. Multiph. Flow* **28**, 1801–1821 (2002)
23. Zhou, H.S., Abanades, S., Flamant, G., Gauthier, D., Lu, J.D.: Predicting heavy metal vaporization dynamics in a circulating fluidized bed riser by a Lagrangian approach. *Powder Technol.* **146**, 20–31 (2004)
24. Graham, D.I., Moyeed, R.A.: How many particles for my Lagrangian simulations? *Powder Technol.* **125**, 179–186 (2002)
25. Levenspiel, O.: *Chemical Reaction Engineering*, 3rd edn. Wiley, Hoboken (1999)
26. Villermaux, J.: *Génie de la réaction chimique*. Technique & Documentation (Lavoisier), Paris (1982)
27. Álvarez, L., Gharebaghib, M., Pourkashanianb, M., Williamsb, A., Riazaa, J., Pevidaa, C., Pisa, J.J., Rubieraa, F.: CFD modelling of oxy-coal combustion in an entrained flow reactor. *Fuel Process. Technol.* **92**, 1489–1497 (2011)
28. Marias, F., Puiggali, J.R., Flamant, G.: Modelling for simulation of fluidized-bed incineration process. *AIChE J.* **47**, 1438–1460 (2001)
29. Khiari, B., Marias, F., Vaxelaire, J., Zagrouba, F.: Use of a transient model to simulate fluidized bed incineration of sewage sludge. *J. Hazard. Mater.* **135**, 200–209 (2006)
30. Liu, H., Gibbs, B. M.: Modelling of NO and N₂O emissions from biomass-fired circulating fluidized bed combustor. *Fuel* **81**, 271–280 (2002)
31. Skreiberg, Ø., Glarborg, P., Jensen, A., Dam-Johansen, K.: Kinetic NO_x modelling and experimental results from single wood particle combustion. *Fuel* **76**, 671–682 (1997)
32. Franck, A., Castaldi, M.J.: CFD analysis of municipal solid waste combustion using detailed chemical kinetic modelling. *Waste Manage. Res.* **32**, 745–754 (2014)
33. Marias, F., Casajus, C.: Torrefaction of corn stover in a macro thermobalance. Influence of operating conditions. *Waste Biomass Valor.* **5**, 157–164 (2014)
34. Ciuta, S., Patuzzi, F., Baratieri, M., Cataldi, M.J.: Biomass energy behavior study during pyrolysis process by intraparticle gas sampling. *J. Anal. Appl. Pyrolysis.* **108**, 316–322 (2014)
35. Turner, I., Rousset, P., Rémond, R., Perré, P.: An experimental and theoretical investigation of the thermal treatment of wood (*Fagus sylvatica* L.) in the range 200–260 °C. *Int. J. Heat Mass Transfer* **53**, 1715–1725 (2010)