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MODELS OF CHEMICAL REACTORS FOR BIOMASS GASIFICATION AND COMBUSTION

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Introduction

Gasification and combustion are technologies widely applied for solid-gas reactions of coal and biomass. Large scale development and optimization require mathematical modeling which, allowing quantitative representation of various phenomena, is a powerful tool for process design, prediction of gasifier performances, understanding of pollutants evolution, analysis of process transients and examination of strategies for effective control. Compared with coal, only a relatively few chemical reactor models have been proposed for biomass. Pyrolysis modeling has been recently reviewed (Di Blasi (2008)) in relation to chemical kinetics and transport phenomena for both single particles and reactors. Also, the models of chemical kinetics and the processes at the level of single particles for gasification and combustion have been examined in the framework of the ThermalNet project (Di Blasi (2006, 2007)). In this report the models currently available for biomass gasifiers and combustors are considered. The analysis is carried out according to the following reactors/systems of conversion: 1) pulverized flame burners and cofiring, entrained-bed gasifiers; 2) packed-bed reactors (grate fired furnaces, fixed-bed combustors, downdraft and updraft gasifiers); 3) rotary kilns; 4) fluidized-bed reactors (bubbling and circulating fluidized bed gasifiers and combustors).

Combustion/gasification of pulverized biomass and co-firing

Cofiring coal or natural gas with limited amount of biomass, often in pulverized form, has been widely implemented in large scale plants (Tillman (2000), Sondreal et al. (2001), Sami et al. (2001), Williams et al. (2001), Nussbaumer (2003), Hupa (2005)). Modeling efforts in this direction include the work by Fletcher et al. (2000), Gera et al. (2002), Yin et al. (2004), Backreedy et al. (2005), Zahirovic et al. (2006), Ma et al. (2007). The usefulness of Computational Fluid Dynamics (CFD) in the design and optimization of pulverized coal fired boilers of various configurations is widely recognized and the most commonly used equations and models have been reviewed by Veynante and Vervisch (2002). Mathematical models are generally based on commercial CFD codes (FLUENT or CFX), where the gas flow is described by the time averaged equations of global mass, momentum, enthalpy and species mass fractions. Different global mechanisms take into account the combustion of volatile species where the effect of turbulence on the reaction rate is modeled with the eddy dissipation turbulence chemistry interaction model (for instance, one (Ma et al. (2007)) or two (Yin et al. (2004)) step mechanisms). The standard k- ϵ model is used for turbulence closure. Radiative heat transfer in the gas phase is generally described according to the Discrete Ordinate Radiation model. The particle phase equations are formulated in a Lagrangian frame and the coupling between the phases is introduced through particle source in the Eulerian gas phase equations (Eulerian-Lagrangian approach). Chief differences among the various treatments consist in the particle-related models.

Fletcher et al. (2000) use an Eulerian-Lagrangian CFD approach to describe gasification of biomass (sawdust or cotton gin waste) in an entrained bed reactor. Particles are assumed to be spherical with appropriate average diameters. The in-homogeneity in the feed is represented by a distribution of particle sizes. Particle heating takes into account the contribution from convection (Ranz-Marshall correlation), latent heat and heat of gasification but spatial gradients are ignored. Pyrolysis uses a prescribed time constant of volatile release with mass fraction of gaseous components given by empirical data depending on the composition of the biomass. Char conversion combines mass diffusion and intrinsic (first-order rate) kinetics (activation energies of 179kJ/mol for gasification and 83kJ/mol for combustion). Simulations provide information about gas composition and temperature fields on dependence of operating conditions, although on qualitative basis only.

A transport model for biomass particle combustion coupled with an Eulerian-Lagrangian CFD treatment to simulate a utility boiler (co-firing biomass in pulverized coal boilers) is presented by Gera et al. (2002). The particle model is coupled with the gas phase processes in a pulverized coal burner, modeled by a commercial CFD code. A Lagrangian formulation is used for the particle phase and the coupling with the gas phase is made via production terms. The biomass particle is treated as a coupled system for devolatilization and combustion. To describe the effects of large length/diameter ratio on the temperature gradients, the unsteady two-dimensional version of the heat conduction equation for cylindrical particles is used for the first stage. The one-step devolatilization reaction is first order in the amount of volatile released, as determined from proximate analysis, with guessed values of the kinetic parameters. The particle diameter (and density) is related, by means of a shrinkage factor, to the current amount of volatiles still retained by the particle. Once the devolatilization process is terminated, combustion occurs at the external particle surface and is controlled by oxidant diffusion and corrected by an enhancement factor to take into account the effects of non spherical shape. The char density is constant, while variations in the particle mass cause a continuous reduction in the diameter. Together with the cylindrical particle model, described above, a simplified model based on the assumption of perfectly stirred system (absence of spatial gradients) is also examined. It is found that, due to a large surface area, the transport model for the particle gives rise to shorter burn-out times. Shape effects are important for the particle trajectories and residence times. For a given volume, the sphere presents the minimum surface area. The cylindrical or ellipsoidal shape, typical of biomass particles, results in a larger surface (when compared with a sphere of equivalent volume). This enhances oxygen diffusion towards the char combustion zone, thus affecting both ignition and burn-out times. Compared with coal, it appears that much larger sizes of biomass particles can be used without increase in unburned carbon in fly ash, owing to the higher content of volatile matter and aerodynamic (shape) factors which allow for longer residence times inside the boiler.

Yin et al. (2004) model co-firing straw with natural gas in 10m long wall-fired burner. The focus of the study is on design aspects and non-spherical shape of biomass particles. For the latter two cases are simulated: (1) the particles are dense or hollow cylinders and (2) the non-spherical particles are simplified as equal-volume spheres, without any modification to the motion and reaction following the absence of spherical shape. The model developed to track non-spherical particles in two-phase flows developed by Yin et al. (2003) is used to predict the motion of non-spherical biomass particles. A specific drag correlation is combined with an additional lift due to particle non-spherical shape and the virtual mass force due to relatively light biomass particles (in addition to gravity and pressure-gradient force). The processes of heating, devolatilization and surface combustion are then modeled taking into account the actual surface area and the surface average oxygen mass flux. In the case (2) no modifications are introduced in the motion and combustion of spherical particles, as assumed in CFD codes.

Intra-particle gradients are neglected. Heating takes place by convection and radiation. Devolatilization is described by a one-step first order reaction ($A=1 \times 10^6 \text{s}^{-1}$, $E=7.4 \times 10^7 \text{J/kmol}$) with variations in the particle diameter according to a swelling factor. The sequential combustion of char is a diffusion-limited surface reaction. The particle size remains constant but the density decreases as combustion proceeds. Simulation results show a strong coupling between particle motion and particle combustion which are also highly dependent on the particle shape. These effects are dominant and should be properly taken into account, in particular the non-sphericity for producing accurate predictions (the importance of shape and size distribution functions in the predictions of processes involving biomass has also motivated the detailed physical characterization (straw) carried out by Rosendahl et al.

(2007)). The analysis also indicates some design issues which can improve the biomass combustion efficiency.

Zahirovic et al. (2006) couple a submodel for solid devolatilization with the commercial CFD software FLUENT to simulate pulverized biomass combustion. Simulations consider both two- and three-dimensional systems. The model results are particularly useful to explain the trends in the temperature field and the ash slagging phenomena.

Ma et al. (2007) model the combustion of pulverized wood in a 1MW test facility consisting of a single burner and a combustion chamber with an over-fire air system. Four distinct processes are modeled for the particles (sizes of 90-1500micron, flat chips and particles of cylindrical shape with aspect ratio in the order of 10), that is, drying, volatile release, volatile combustion and char combustion. Particle tracking is made according to the momentum equation with empirical formulae to calculate the drag for non-spherical shapes. Intra-particle gradients are neglected. Heating takes place by convection (based on the particle Reynolds number and the Prandtl number of the continuous phase) and radiation (P1 model). Moisture evaporation is diffusion controlled. Devolatilization is described by a one-step finite-rate reaction with $A=6 \times 10^{13} \text{s}^{-1}$ and $E=2500 \text{kJ/mol}$ which, as pointed out by the authors, present a significant diversity with typical literature values. An interesting feature of this study is that potassium evolution is taken into account (it is worth noting that previous work of this research group on co-firing pulverized coal and biomass modeling (Backreedy et al. (2005)) uses the devolatilization kinetics proposed by Chen et al. (1998)). It is assumed to be released at the same rate as volatiles and to form KOH (the low chlorine content of wood justifies the negligible formation of KCl). Similar to coal, NO can be formed by the thermal mechanism or from fuel NO. Fragmentation of char particles is neglected and combustion kinetics is used as previously determined for coal with a pre-exponential factor increased by a factor of 4 to take into account the higher reactivity. Results show that particle trajectories and residence times are significantly affected by the shape. Consistent with experimental observation, larger particles tend to fall to the bottom, many near the burner, while others follow the gas flow field out through the furnace. Particles heat up to 1500K in less than 0.25s after feeding. Temperature and CO₂ concentrations at the furnace exit show values close to those measured. It is also observed that large part of volatiles and potassium are released at 973K. Although there are high simplifications in the description of the various processes, it is interesting to note that inclusion of potassium release permits to evaluate its concentration in the gas phase. Thus this model represents a basis for the development of ash deposition models.

The modeling efforts on pulverized biomass gasification/combustion or on co-firing biomass with natural gas or coal show that comprehensive Eulerian-Lagrangian CFD treatments, based on commercial software, are coupled with simplified particle models. Simplifications are applied for both chemical kinetics (devolatilization and char conversion) and transport phenomena. Simulation results indicate that both intra-particle gradients and shape and size play an important role. Therefore, these aspects should be properly taken into account. Issues which require further investigation include, NO_x formation, alkali metal release and particle processes (more accurate chemistry, drying, swelling, fragmentation, etc.). Commercial CFD codes, applied to simulate solid fuel combustion and gasification, present low performances when applied to follow particles completely through a system (Syred et al. (2007)), which can be improved by incorporating appropriate sub-models for particle size distribution and thus fragmentation during the conversion process. These issues are reviewed (Syred et al. (2007)) and the need is evidenced of developments to better reflect actual fragmentation conditions in different experimental systems.

Combustion and gasification of biomass in packed beds

Several models for the combustion and gasification of biomass in packed beds and the combustion in grate fired furnaces have been proposed. These models can be classified into two main categories (Yang et al. (2005), Johansson et al. (2007)). The first comprises continuous-medium models, where the bed is treated as a porous medium consisting of one solid and one gaseous phase, each of which can be described as a continuum in a global coordinate system ("porous medium approximation"). This is the most extensively used treatment. A difference among the available models can be found in the description of either the packed bed alone, to simulate fixed-bed combustion, or the packed bed coupled with the gas-phase processes (free board) to simulate combustion on a moving grate. The level of complexity of both the packed bed and the free board of the moving grate are highly variable among the various authors. The second category comprises models accounting for intra-particle gradients, where again different approximations are employed at the level of the single particle. Minor categories, as discussed by Yang et al. (2005), are those of models of neighboring-layers, representing fuel, drying, pyrolysis and ash, and well stirred models, where the bed is simulated by a cascade of well stirred reactors.

Model based on the porous medium approximation include, for combustion, the works by Fatehi and Kaviany (1994, 1997), Zhou et al. (1995), Saastamoinen et al. (2000), Gort and Brouwers (2001), Shin and Doi (2000), Saastamoinen et al. (2000), Knaus et al. (2000), Scharler and Obernberger (2000), Peters (2002), Kaer (2004,2005), van den Lans et al. (2000), Zhou et al. (2005, 2006), Yang et al. (2003, 2004, 2005a, 2005b, 20006, 2007). Some models are essentially focused on the solid-phase processes whereas others privilege the gas-phase combustion and the solid phase processes are simply approximated by means of a boundary condition. This is specified either by using experimental data collected near the bed or by numerical simulation of the fuel bed combustion process using a stand-alone bed model.

Some solid phase models essentially describe the quasi-steady-state spread of propagation of the ignition front downwards against the air flow in a fixed bed of wood particles (Fatehi and Kaviany (1994, 1997), Zhou et al. (1995), Saastamoinen et al. (2000), Gort and Brouwers (2001))), using simplifications in the formulation of transport equations and solution methods. Fatehi and Kaviany (1994) investigate counterflow combustion in a packed bed of wood particles assuming that the heterogeneous reactions between char and oxygen are the dominant mechanism and the gas and solid phase are in thermal equilibrium. The fuel and oxygen limited regimes are simulated together with the characteristics of the reaction front. In a successive study (Fatehi and Kaviany (1997)) allowance is made for the local thermal and chemical non equilibria between the phases. The role of the air pore velocity and the homogeneous reaction rate in the front speed, the adiabatic final temperature, the degree of solid consumption and the un-burnt volatiles concentration in the post gas-phase oxidation region, are examined parametrically. Volatiles are produced from wood pyrolysis, according to a volumetric solid-phase reaction. Gas phase reaction becomes dominant over the heterogeneous reaction at high air pore velocities, thus reducing the rate of solid consumption. In Saastamoinen et al. (2000), neglecting the initial transients, the case of the ignition wave stabilized to a constant velocity is investigated (propagation of a thermal wave in an infinite medium). Owing to the counterflow air, the main mechanism causing the front propagation is assumed to be radiation, although conduction and gas mixing near the flame front are also important. Moreover, as turbulent mixing and combustion near the flame are difficult to model, the local absorption of energy in the bed is assumed to be directly proportional to the local heat flux. Then the heat flux from the burning particles through the bed decays

exponentially with distance. In (Gort and Brouwers (2001)) an activation energy asymptotics method is exploited to obtain asymptotic solutions for the three differential equations for the transport of heat, solid reactant and gaseous reactant. Also an expression for the propagation of a reaction front through a porous bed of municipal solid waste is obtained using a one-dimensional energy conservation equation (Zhou et al. (1995)). The reaction front is divided into two parts, an ignition front where large part of solid fuel gasification takes place and a flaming front where gas phase oxidation occurs. The calculation of the propagation velocity as a function of a characteristic ignition temperature is based on heat transfer mechanisms (convection, conduction, radiation) towards the virgin fuel. For a control volume at the ignition front the Semenov thermal explosion theory is used to determine the characteristic ignition temperature.

Combustion of waste above a grate is modeled by means of a one-dimensional bed of particles by Shin and Choi (2000), using separate enthalpy equations for the solid and the gas phase. The solids in the bed experience the sequence of events typical of solid fuel combustion: moisture evaporation (mass transfer control with moisture at the particle surface at the saturation condition with the bed temperature), devolatilization (two competitive reactions for the formation of char and volatiles), char oxidation (combination of mass transfer control and intrinsic chemical kinetics), volatile combustion (two separate reactions for CO and the remaining combustible fraction), cooling of the ash. The mass of the bed in the control volume exchanges heat with the material in the upper and lower control volume via conduction, convection and radiation (two-flux model). As the reaction progresses, volume and density of the control volume change.

The propagation of an ignition front across a packed straw bed is simulated by van der Lans et al. (2000). A homogeneous two-dimensional model is developed where the gas flows in the y-direction and enters the bed through the bottom plate. Gas and solids are assumed in plug flow. Thus the model consists of the steady enthalpy conservation equation coupled with mass balances for O₂, CO, CO₂ and the total gas flow. Devolatilization is described by a first-order reaction followed by char oxidation with a first-order rate in the oxygen concentration. Model results are compared with laboratory-scale experiments (gas species concentrations, bed temperature and ignition front propagation rate).

Kaer (2005) proposes a one-dimensional model to simulate straw combustion on slow-moving grates (vibrating grate). The bed model is apt to predict: 1) release and oxidation of volatile species, oxidation of the char, solid and gas temperatures and species concentrations (O₂, CO, CO₂, H₂O). The model can be considered an improvement of that proposed by van der Lans et al. (2000), because it removes the assumption of local thermal equilibrium and is experimentally validated. Apart from producing the boundary conditions for the possible simulation of the free-board dynamics, two different combustion modes are observed, controlled by the combustion air temperature and the mass flow-rate. The first mode is characterized by a devolatilization front that moves downwards followed by an upward moving char oxidation front. In the second mode, devolatilization and char oxidation initiate at the grate and moves upwards. The ignition velocity is significantly faster in the second mode and the gas temperature is lower.

A one-dimensional and unsteady model for straw combustion in a fixed bed is presented by Zhou et al. (2005). The model takes into account moisture evaporation, straw pyrolysis, combustion of volatile species, char oxidation (formation of CO and CO₂) and temperature differences between the solid and the gas phase. Predictions of the detailed structure of the ignition flame front is provided with a flame front thickness about 24-50mm. Good qualitative agreement is obtained between predictions and

measurements as operating conditions are varied. A parametric analysis shows that the effective heat conductivity, straw packing conditions and heat capacity of the straw are the most important parameters. The straw-bed model is also extended to simulate the formation and reduction of nitric oxide (Zhou et al. (2006)). Twenty chemical reactions are included, of which twelve belong to the fuel nitrogen reaction mechanism. Volatile nitrogen is assumed to be NO, NH₃, HCN and HNCO, and char nitrogen is converted to NO during char oxidation. Simulation and measurements are combined to find effective conditions for reducing NO emissions.

Yang et al. (2003, 2004) present a one-dimensional unsteady model of solid fuel combustion in a packed bed of wood or waste particles. Moisture evaporation is dominated by mass transfer whereas a one-step finite rate reaction describes solid devolatilization. Volatile hydrocarbons are assumed to be a single product oxidized to give CO and H₂, which are then combusted to form CO₂ and H₂O, respectively. The burning of volatile hydrocarbons is limited not only by the reaction kinetics but also by the mixing rate of the gaseous fuel with the under-fire air. The char combustion rate is described by rate constants due to chemical kinetics and diffusion producing CO and CO₂ (the product ratio presents an Arrhenius rate law). The fundamental mechanisms of heat and mass transfer are taken into account by the mass and energy conservation equations for the system (radiation described by a two-flux model). The main purpose of the work (Yang et al. (2003,2004)) is to simulate the effects of the initial moisture content, distribution of the air flow and the devolatilization rate on the combustion process. Apart from the profiles of the dependent variable, the bed behavior is simulated in terms of ignition time, burning rate, reaction zone thickness, peak flame temperature, combustion stoichiometry and unburned gas emissions at the bed top. It is found that the devolatilization kinetics has a significant effect on the ignition time, peak flame temperature, CO and H₂ emissions and amount of char burned during the combustion stage. The size of the reaction zone is between 20-55mm and is affected by the moisture content. Volatile release and char burning are enhanced by successively higher flows of primary air until a critical point when an inversion occurs. Higher primary air flows also reduce the char fraction burning in the final stage of pure combustion, shift combustion in the bed to a more fuel-lean environment and reduces CO emissions.

Yang et al. (2005a) put into evidence that particle mixing caused by grate movement in a packed bed of biomass particles is an important process and propose a diffusion model. The diffusion model is incorporated in the bed model previously developed by the same research group. Experiments are also carried out to measure the diffusion coefficient. As expected, simulations indicate that mixing enhance the propagation speed of the reaction front but, when excessive, the ignition is delayed and bed extinction may occur. Estimated values of the diffusion coefficient are between 1.8-6cm²/min. The complete model is also used to simulate the effects of fuel size, density, LCV on biomass combustion (Yang et al. (2005b) and the substoichiometric conversion of biomass and waste (Yang et al. (2006)). Both studies compare simulations and experiments.

While the usefulness of CFD tools in the design of pulverized coal fired boilers is fairly well established and several applications are also available for biomass, the description of grate-fired boilers is more complicated. A crucial issue is the modeling of the processes taking place in the fuel layer, which need to be coupled with the CFD treatment of the gas-phase processes. Applications of CFD models are the works by Scharler and Obernberger (2000), Kaer (2004), Strohle et al. (2006), Yang et al. (2007), Klason and Bai (2007), including the aspects related to turbulence modeling (Knaws et al. (2000), Scarler et al. (2003)).

The commercial CFD software FLUENT has been applied (Scharler and Obernberger (2000)) for the optimization of the geometry of the combustion chamber and secondary air nozzles of a biomass grate furnace. Apart from the standard treatment of gas-phase processes, a semi-empirical model is introduced for the evaluation of the mass and energy fluxes from the fuel bed to the gas phase in terms of boundary conditions. Results confirm the potential of CFD models for the optimization of furnace geometry and air distribution. In particular, the visualization of dead zones permits the minimization of the volume of the furnace. CFD predictions of a straw-fired grate boiler, based on the commercial software CFX (steady two-dimensional equations solved with the SIMPLE algorithm, k- ϵ turbulence model, discrete transfer model for radiation and the eddy-break-up and a two-step combustion mechanism with CO as the intermediate species), are presented by Kaer (2004). The solid-phase processes are described by means of a boundary condition based on the solution of a simplified model. Good agreement is obtained between predictions and measurements of temperature and species concentrations. Poor mixing in the furnace is found to be the main cause of high emission levels and high amounts of unburned carbon in the fly ash.

A small-scale grate-fired furnace with wood pellets has been modeled by Klason and Bai (2007) with the focus on the gas-phase processes and, more specifically, on NO mechanisms and effects of air distribution. A semi-empirical model for the bed is coupled to a gas-phase combustion model based on the Reynolds averaged Navier-Stokes equations for reacting flows and the standard k- ϵ turbulence model. Four global reactions are used to model the combustion of light and heavy hydrocarbons, carbon monoxide and hydrogen. The rates are assumed to be controlled by the mixing rate according to the eddy dissipation concept. Different paths for the NO emissions are investigated including the thermal NO, the fuel-NO and the NO from N₂O intermediate mechanisms. Radiation heat transfer is described by the P1-approximation. The bed model is based on the following approximations: no spatial gradients exist across the bed and the state of particles is homogeneous; volatile species comprise CH₄, tar, CO, H₂, O₂, CO₂, H₂O and N₂; all the fuel nitrogen is converted to HCN and NH₃ and the molar ratio between the two is constant and equal to 0.5; four of the eight volatile species yields are known from the experiments; the temperature or the heat transfer between the bed and the gas phase are known. Simulation results, compared with temperature and species measurements, indicate that combustion is controlled by the turbulence associated with secondary and tertiary air injection.

Models for the solid and the gas phase are presented by Strohle et al. (2006), Yang et al. (2007). Strohle et al. (2006) present a two-dimensional model for wood particles moving, with a constant velocity, on a grate. They undergo drying, pyrolysis and char burnout while the gas phase processes are modeled by a CFD code. It is found that the main heat transfer mechanism is radiation from the gas phase combustion towards the particle bed. Simulation results appear to be qualitatively correct but experimental validation is lacking. Yang et al. (2007) investigate the operation of a 38MWe straw-burning power plant using a vibrating-grate furnace. The model consists of two sections, one for in-bed combustion and another for out-of-bed combustion. The bed model essentially comprises the two-dimensional unsteady mass and energy conservation equations and is coupled to the gas phase processes as described by the commercial code FLUENT. The assumptions made in the description of the bed are common to previous treatments including particle mixing effects. The simulations appear to be consistent with experimental observation. The sub-stoichiometric combustion of straw and the short residence times of volatiles in the bed result in the release of the fuel-N in the form of NH₃ (very little NO is formed in the bed), so that NO formation mainly occurs in the extra-bed regions. High moisture contents of straw produce difficulties in plant operation due to poor mixing between volatiles and

secondary air and reduce furnace temperatures. Moisture contents above 25% can cause severe deterioration of the plant operation by high CO emissions.

Numerous models have been proposed for fixed-bed gasifiers, given that this technology is applied for 89% of the coal gasified in the world (entrained beds contribute for 10% and fluid-beds only for 1%) (Radulovic et al. (1995)). The state of the art for coal conversion has been carefully reviewed by the Advanced Combustion Engineering Research Center of the Brigham Young University (Provo, UT) (Hobbs et al. (1993)). The common features adopted by the different models have been identified and include: 1) single shape and size of the particles, 2) no momentum transfer, 3) constant porosity of the bed, 4) heat and mass transfer coefficients for non reacting systems, 5) instantaneous drying, 6) instantaneous or highly simplified solid devolatilization, 7) uncertainty on the intrinsic kinetics of heterogeneous combustion and gasification reactions, 8) no homogeneous gas phase reaction, apart from the water-gas shift equilibrium, 9) steady, one-dimensional equations, 10) limited model sensitivity analysis and validation. The authors of the review also point out that "model development has not reached the point where significant use is made in process development for coal utilization", but some successive analyses presented by the same research group (Radulovic et al. (1995), Ghani et al. (1996)) have contributed significantly in this issue through models which remove the assumptions 3), 5), 6) and 10). Also, the study by Monazam and Shadle (1998), aimed at the formulation of engineering correlations for countercurrent coal gasification, and those by Hallett and coworkers (Cooper and Hallett (2000), Ryan and Hallett (2002)) for char gasification should be mentioned.

Kinetics-free, equilibrium models can predict the exit gas composition, given the solid composition and the equilibrium temperature, but they cannot be used for reactor design (Buekens and Schoeters (1985)). Chemical reaction kinetics and transport phenomena have been properly coupled to model conventional (Groeneveld and van Swaaij (1980)) and stratified (Manurung and Beenackers (1994)) downdraft gasifiers for biomass. However, the description of the "flaming pyrolysis" (Reed and Markson (1985)), that is biomass pyrolysis and combustion of volatile pyrolysis products, is still based on equilibrium models or on highly simplified treatments, which assume the existence of a stable combustion zone with infinitely oxygen conversion rate near the air inlet. Furthermore, these models describe steady state conditions. Thus they do not allow the prediction of the dynamic behavior of stratified gasifiers and of the different modes of stabilization of the reaction front and thus the size of the reduction zone. One-dimensional and unsteady models of stratified concurrent (downdraft) reactors have been proposed by (Di Blasi (2000)) for biomass gasification and Gobel et al. (2007) for lignocellulosic char gasification. Both models use the porous medium approximation.

In the model by Di Blasi (2000) heat and mass transfer across the bed are coupled with moisture evaporation, biomass pyrolysis, char combustion and gasification, gas-phase combustion and thermal cracking of tars. Numerical simulation has allowed to predict the influence of model parameters, kinetic constants and operational variables on process dynamics, structure of the reaction front and quality of the producer gas. In particular, two different stabilization modes of the reaction front have been determined. For high values of the air to fuel ratio and of the primary pyrolysis rate, the process is top-stabilized, resulting in a high conversion efficiency and good gas quality. As the air flow is decreased below a critical limit value, the reaction front becomes grate-stabilized. The two different configurations are largely determined by the gas-phase combustion of volatile pyrolysis products. Finally, the predictions of the gas composition and the axial temperature profiles are in agreement with experimental data. Gobel et al. (2007) present a model for co-current fixed-bed char gasifier which is the limiting unit in the operation of a multi-stage gasification system. The model takes into account the

main features of the conservation equations for mass and energy for a one-dimensional unsteady system. Furthermore chemical equilibrium for the gas phase (H_2O , H_2 , CO_2 and CO) and Langmuir-Hinshelwood kinetics for char gasification are assumed. The model is applied to predict the stationary performance of the gasifier and its response to changes in operating parameters and to operate a comparison with experimental results. In particular, the model has been useful for finding an efficient control strategy for the operation during load changes that was successively implemented in the design and operation of a gasification plant.

A highly simplified description has been proposed for the countercurrent (updraft) configuration of gasifiers, specifically applied for the gasification of bundled jute sticks (Kayal and Chakravarty (1994)). More recently a more detailed model has been proposed by Di Blasi (2004) for wood, again based on the porous medium approximation. It is a one-dimensional, unsteady mathematical model which couples heat and mass transport with wood drying and devolatilization, char gasification, and combustion of both char and gas-phase species. The model is used to simulate the structure of the reaction fronts and the gasification behavior of a laboratory scale plant as the reactor throughput and the air to wood (or char) weight ratio are varied. It is observed that a wide zone, acting essentially as a countercurrent heat exchanger, separates combustion/gasification from devolatilization/drying. Moreover, the former zone presents interesting dynamic patterns driven by the highly variable solid/gas heat transfer rates. For a constant air to wood weight ratio, the gasification process is improved by increasing the reactor throughput as a result of higher temperatures, in spite of the simultaneous reduction in the amount of char generated from wood devolatilization. In fact, an increase in the air to wood (or char) ratio always lowers the efficiency of the gasification process. Finally, good agreement is obtained between predictions and experiments for the axial temperature profiles and the composition of the producer gas.

Single particle effects in the description of packed-bed combustion of biomass are taken into account by several authors (Peters (2002), Bruch et al. (2003), Wurzenberger et al. (2002), Yang et al. (2005c), Thunman and Leckner (2003,2005), Johansson et al. (2007a,b)), whereas for gasification the model by Yang et al. (2006) should be mentioned. Peters and coworkers (Peters (2002), Bruch et al. (2003)) present a model for the combustion of packed bed of single particles and carry out the experimental validation at the level of both particle and reactor. Each particle has its own shape and properties and the main stages of the combustion process are described by means of one-dimensional and unsteady conservation equations for mass and energy (convection, diffusion/conduction and chemical reactions). Particles give rise to a solid and a gas (void) phase. Heat and mass transfer couples the processes of the gas phase to those of the particles, although the boundary conditions instead of using the actual mass/heat fluxes for the two phases are based on global coefficients for the gas-phase side. Simulations are not used to understand the interaction between the two phases or to provide detailed information on process dynamics.

A combined transient single (spherical) particle and fuel-bed model is also presented by Wurzenberger et al. (2002). The fuel bed model is discretized in the axial direction. For each cell one particle is chosen and discretized in the radial direction. Thus the entire bed is divided into two subsystems, that is, the gas phase inside the bed and the individual particles ("transient 1-D+1-D model"). Again the chief heat and mass transfer phenomena and relevant chemical reactions (three competitive reactions for primary pyrolysis, cracking of primary tars, heterogeneous reactions of char conversion, gas phase water gas shift, homogeneous combustion of CO , H_2 , CH_4) are properly taken into account. The grid remain spatially unchanged during conversion and the shrinkage is taken into account by variations in

the porosity which can reach a unity value. Comparison of the single particle model results with measurements shows good agreement. Packed bed simulations indicate that the various conversion mechanisms do not occur simultaneously at a given bed height. The time for complete burnout of the bed is affected by particle properties and operating conditions (primary air flow rate and temperature, bed height and temperature of the combustion chamber).

A different approach is used by Yang et al. (2005c) to describe the inhomogeneous nature of the bed and the effects of thermally thick particles. The bed consists of particles and the voids between them. In the discretization of the bed three different types of cells are introduced: void cells, boundary cells and inner cells. The void cells describe the gas flow while the inner cells are representative of the interior of the particles. Boundary cells are solid-phase cells adjacent to the gas flow around the particle outer surfaces. In this way, a particle is represented by a set of inner and boundary layer cells and the bed an assembly of inner, boundary and void cells. For each cell the conservation equations are applied and different assumptions are made depending on the cell type. For example, with reference to heat transfer, for an inner cell only heat conduction is taken into account. For a boundary cell, heat convection, conduction and radiation are described. For the void cells, in addition to the three heat transfer mechanisms, turbulence effects are also included. Experimental analysis and simulation results are used to clarify the effects of particle size on the combustion characteristics of the packed bed. Smaller particles present shorter ignition times and faster burning rates. The size of the reaction zone is also thinner and emission levels of CO and CH₄ are higher. Transients are more evident for larger particles which are also characterized by higher combustion temperatures and H₂ concentrations in the flue gas. The model (Yang (2005c)) has also been applied to simulate the gasification of char in a countercurrent reactor (Yang et al. (2006)). It appears that the gasification process is affected by both chemical kinetics and mass transfer between the solid and the gas phase and that the predicted gas composition is significantly dependent on the model parameters.

Thunman and Leckner (2003, 2005) propose a model for a packed-bed combustion consisting of gaseous and solid phases. The solid phase comprises particles of the same size and optional shape. The two media are considered as one-dimensional continua. To take into account the effects of thermally thick particles, the source terms that express the conversion of the solid phase are treated by means of a single particle model previously developed. The particle model is one-dimensional and describes the temperature profiles and the release of moisture and volatiles. The gas phase equations disregard momentum conservation and are steady (small pressure drop across the bed and short residence times of volatiles compared with the conversion times of the solid phase). The bed porosity is assumed to remain constant and the gas to be transparent for radiation (radiation in the solid phase is described by a two-flux model). Other processes taken into account include elutriation of solids, solid mixing in the bed expressed as dispersion, and heat transport by diffusion of gaseous species or by dispersion of solids. The model is applied to simulate co-current and countercurrent fixed-bed combustion (Thunman and Leckner (2003)) and the influences of size and density for a bed ignited at the boundary opposite to the air inlet (Thunman and Leckner (2005)). Particle density plays only a minor role, whereas the particle size has a significant influence on the packed bed combustion. The propagation rate of the reaction front is lower for thick particles which also show significant temperature differences between the particle surface and the gas and the processes of drying, devolatilization and combustion overlap. Improvements in the model are represented by the more recent works of the same research group (Johansson et al. (2007a,b)). In this case a two-dimensional model for the particles is coupled with a one-dimensional model for the bed. The two-dimensional description takes into account the dependence of the temperature profile both on the distance from the surface and the height of the

bed. The one-dimensional grid, for the gradients of gas-phase variables in the bed and the surface temperature of the temperature requires a cell size much smaller than the diameter of the fuel particle. The bed is assumed to consist of spherical particles of the same size. The solid and the gas phase are treated separately in the absence of local thermal equilibrium, reproducing in the main features the same treatment previously proposed. The shrinking particle model consists of a two-dimensional transport equation for heat conduction and the energetics of drying and devolatilization. The boundary condition is the surface temperature, given by the temperature of the solid phase in the porous bed model. Char combustion takes place on the particle surface. The coupling between the bed and the particle model is carried out through three parameters, obtained from the particle model and given as inputs to the bed model: a heating ratio, an effective drying temperature and an effective devolatilization temperature, expressed as functions of the surface temperature. Comparison of the simulation results with those obtained from a model based on the porous media approximation show significant differences in the release rates of moisture and volatiles and the temperature profile in the bed. However, given a range of particle sizes of 5-20mm, the effects are relatively small. The uncertainty of the input parameters is also found to have a small effects of the predictions. From the quantitative point of view, good predictions are obtained for the ignition rate and the maximum temperature. Finally, gas composition is highly influenced by the devolatilization model.

Solid combustion in rotary kilns

A comprehensive model of a rotatory kiln should describe the processes that occur at different spatial scale and in different phases (Marias (2003)). Solid pyrolysis is driven by intra-particle heat and mass transfer, by heat transfer within the burning bed which, in turn, is controlled by bed motion, combustion of volatile matter generated from pyrolysis and radiation. Rotary kilns are employed by industry to carry out a wide variety of material processing and for waste treatment. A significant effort has been made for the description of gas phase phenomena occurring within a rotary kiln, usually based on commercial CFD software (Khan et al. (1993), Leger et al. (1993), Jakway et al. (1996)). Finite difference approximations are used for the solution of the flow field. The Reynolds averaged Navier-Stokes equations coupled with the Reynolds-averaged governing differential equations of continuity, energy and species are solved in a discretized form. The standard k- ϵ turbulence model is employed. The pressure-linked continuity and momentum equations are solved using the Semi-Implicit method for Pressure-Linked Equations Consistent solution algorithm. Successive improvement (Jakway et al. (1996)) also includes radiation (Discrete Ordinate Method) and soot in the heat transfer analysis. The rate of the gas phase reaction is assumed to be turbulent mixing rate limited and described according to the eddy breakup model. The CFD approach does not allow for the modeling of the burning bed of solids. The heat transfer from the freeboard gas to the bed of the rotary kiln is described by the model by Boateng and Barr (1996). The model for the solid incorporates a two-dimensional representation of the bed transverse plane into a one-dimensional plug-flow model for rotary kiln. The resulting quasi-three-dimensional model shows better prediction capabilities of the conditions within the bed with the necessity of CFD description of the gaseous reactive phase of the freeboard. A simplified model of the solid phase processes is, on the contrary, proposed by Marias (2003). Indeed, the main focus of this study is the coupling between the solid phase model and the CFD description of the gas phase processes.

These studies show that the main features of solid fuel combustion in rotary kilns have been modeled but the applications are essentially focused on waste materials. The current achievements provide a

sound basis for possible developments for the aspects related to solid-phase processes, in particular decomposition reactions and heterogeneous conversion of char.

Combustion and gasification of biomass in fluidized-bed reactors

A significant number of papers has been published on models for fluidized-bed conversion of coal whereas, excluding kinetic-free equilibrium calculations to estimate the final composition of the gas, only in a relatively few cases biomass has been considered. However models are available for both gasification with bubbling fluidized beds (Raman et al. (1981), Bilodeau et al. (1993), Jiang and Morey (1992), Jennen et al. (1999) Hamel and Krumm (2001), Fiaschi and Michelini (2001), Sadaka et al. (2002a,b), Radmanesh et al. (2006)) and circulating fluidized beds (Liu and Gibbs (2003), Corella and Sanz (2005), Sanz and Corella (2006), Corella et al. (2006)) and combustion (Marias et al. (2001), Khan et al. (2007a,b)). Bubbling fluidized-bed models are always based on the two-phase flow theory of fluidization for the description of the process hydrodynamics (particle-lean bubble phase surrounded by a particle rich emulsion phase).

An unsteady, one-dimensional model of a fluidized bed gasifier is proposed by Raman et al. (1981). The equations for the bed are formulated according to the two-phase fluidization theory with instantaneous devolatilization and finite-rate gasification kinetics (char gasification and water gas shift reaction). Comparison with measurements indicate that cracking and reforming reactions involving the volatiles produced during devolatilization should be included in the model.

A one-dimensional, steady-state model for a fluidized-bed biomass gasifier is presented by Jiang and Morey (1992). Pyrolysis, oxidation and combustion taking place in the bed are coupled with a freeboard model. The pyrolysis process is assumed to occur instantaneously with amount and composition of products computed from empirical correlations. Heights of the oxidation and gasification zones define the domains for the different models. The section of oxygen depletion is computed by observing that this is a very fast process occurring around the feed port. The gasification model is based on the two-phase fluidization theory and involves the concentration of eight gas species, each of which is described with a system of two differential equations, one for the bubble phase and the other for the dense phase (CO₂, H₂O, tar, C₂H₄, N₂, H₂, CO, CH₄) with a combination of intrinsic kinetic rates and diffusion control. The gasification model is experimentally validated although in some cases temperature, energy content of the gas and fuel conversion predictions are poor. Acceptable predictions are obtained for particle entrainment and gas composition. From a sensitivity analysis it appears that fuel pyrolysis, char gasification and tar cracking and interphase exchange are in descending order of importance to the model.

Bilodeau et al. (1993) propose a one-dimensional steady model for a fluidized-bed gasifier. It includes axial variations of concentrations and temperature in the bubble and emulsion phases. Oxidation reactions occur instantaneously and proceed until all the oxygen available has been consumed. The products of fuel devolatilization enter in the emulsion phase. An equilibrium calculation, based on the Gibbs free energy minimization, determines the composition of the devolatilization products. Kinetics of solid-gas gasification reactions as well as of gaseous phase reactions are finite-rate. The energy balance is solved locally for each vertical volume element and globally on the reactor by iteration on the temperature at the bottom of the bed. Using as adjustable parameter the heat transfer coefficient at the wall, the weighting of the kinetics of the water-gas shift reaction and the fraction of biomass carbon remaining as char after devolatilization, the simulation results are compared with measurements carried out for a 50kg/h reactor.

The model by Hamel and Krumm (2001) takes into account the bed and freeboard hydrodynamics, solid fuel drying and devolatilization and the main gasification reactions. Although details of the model are not provided and a significant part of the results deal with coal gasification, overall carbon conversion, temperature and gas composition are compared with literature data.

Fiaschi and Michelini (2001) divide the one-dimensional and steady-state bubbling fluidized bed reactor in vertical elemental cylinders according to a two-phase fluidization theory up to the freeboard zone where no reaction is assumed to occur. The two phases for the bed include the relevant gasification reactions, mass transfer between the two phases and related properties.

Sadaka et al. (2002a,b) develop a one-dimensional and unsteady model for a bubbling fluidized-bed gasifier based on the two-phase flow approximation. The stages are included of instantaneous devolatilization of biomass (straw), combustion of char at the bottom of the gasifier and gasification in the fluidized bed. The two-phase flow approximation incorporates the phenomena of jetting, bubbling, slugging and dynamic energy and mass balances. More precisely the dilute phase includes jets, bubbles and/or slugs while the emulsion phase consists of an interstitial gas phase and a solid phase (exchange takes place among the various phases). The fluidizing gas enters the bed through nozzles in a jet form (the jets degenerate into bubbles which may form slugs). The model is approximated in terms of finite elements. The gas consists of CO, CO₂, H₂, H₂O, CH₄ and N₂. The number of total moles, which enter the gasifier from the straw volatiles and the gasifying agent are calculated by the minimization of the free energy, so that this is a semi-equilibrium model. A sensitivity analysis complete the study.

Radmanesh et al. (2006) propose a one-dimensional isothermal model for a bubbling fluidized bed gasifier taking into account both the bubbling bed and the freeboard area. It couples the two-phase model for the bed hydrodynamics with the relevant processes of wood gasification. Pyrolysis (primary and secondary pyrolysis according to one-step reactions with kinetic rates not representative of intrinsic kinetics) takes place instantaneously in the feeding zone (solid mixing proceeds more slowly than pyrolysis) with yields of the different products evaluated from literature and used as inputs in the model equations. Particle mixing in the bed is modeled according to the countercurrent back-mixing model. Particle heating occurs in the absence of spatial gradients (sizes below 1mm) with an external heat transfer coefficient provided by the Ranz-Marshall correlation. Reactions take into account the combustion of tar, CH₄, H₂ and CO, the gas phase water gas shift and the heterogeneous gasification (H₂O, CO₂) and combustion of char. Equations are written to obtain the gas concentration and char conversion in the bed. A plug flow model, in series with the bed model, describes the freeboard region (relevant reactions include tar cracking and water gas shift). Simulations, which show acceptable agreement with measurements, confirm the important role played by the pyrolysis step.

Circulating fluidized bed gasifiers for biomass fuels are modeled by Jennen et al. (1999), Liu and Gibbs (2003), Corella and Sanz (2005), Sanz and Corella (2006), Corella et al (2006). The model by Jennen et al. (1999) consists of separate modules for the description of the flow structure, the kinetics of the gasification reactions, the particle size distribution and the energy balance for the reactor. From the point of view of hydrodynamics, the reactor is divided in a dense bed at the bottom of the riser and a dilute bed above it. The bottom dense bed is modeled as a bubbling fluidized bed, according to a bubble and an emulsion phase, while the diluted bed (freeboard) is modeled with the use of a core-annulus structure. Primary pyrolysis gives rise to primary tar, permanent gases and char. Then primary tars undergo secondary reactions to produce permanent gases and a secondary tar. Literature values are

used for the kinetic constants of the finite-rate gasification reactions. Good agreement is shown with the measured pressure drop, temperature profile and gas composition at the riser exit for a 500kW reactor.

Liu and Gibbs (2003) focus their attention on the NH_4 and HCN emission. The circulating fluidized bed gasifier is described by sub-models for biomass devolatilization, tar cracking, gasification reaction and nitrogen chemistry, for a total of forty reactions (kinetics derived from literature). Then hydrodynamics of the riser are modeled assuming a known profile of solid concentration with a plug-flow behavior for both the solid and gas phase. Model predictions show acceptable agreement with the measured values of gas composition, tar and NH_3 emissions. A sensitivity analysis is also presented for the mechanism of nitrogen chemistry.

Corella and Sanz (2005) present a one-dimensional steady steady model which couples heat and mass balance equations with simplified description of hydrodynamics. The main effort is on the selection of a reaction network including twelve steps with kinetic constants carefully selected from literature. Model outputs consists of the axial profiles of temperature and chemical species (H_2 , CO, CO_2 , CH_4 , C_2H_n , H_2O , O_2), gas yield, tar content in the gas and char concentration in the solid. A parametric analysis (Sanz and Corella (2006)) presents the effects of the equivalence ratio, percentage of secondary air flow, location of the secondary air flow and biomass feed rate (and moisture content). The conditions that allow to produce a gas with a low tar content have also been simulated (Corella et al. (2006)).

Marias et al. (2001) present an unsteady model for the fluidized bed incineration of waste composed of wood, cardboard and polyvinyl chloride. Bed hydrodynamics are described by the Werther model (1980) (the existence is postulated of a film between the bubble and the emulsion zone) which permits the description of a diffusion phenomenon from the fuel rich (emulsion) and fuel lean (bubbles) regions. The description of the buffer zone is modified to take into account the removal of the high amount of volatiles, generated from waste devolatilization in the emulsion, by the ascending bubbles (the Werther film is replaced by a two-dimensional reactive zone). The free board region is modeled according to two perfectly stirred reactors for the disengaging height and the post combustion zone. The model is completed by balance equations for the gaseous species and a population balance for the char. It is assumed that drying only affects the internal structure of the solid and results in a decrease of the material density. As a consequence of pyrolysis, the material breaks into a gaseous component (volatiles, nitrogen and sulfur at atomic state) and a solid component (fixed carbon and ash). The heterogeneous combustion of char occurs at the external surface of the particles and is both kinetic and external mass transfer limited. Because the kinetic rate of volatile combustion is very high, the conversion is assumed to be controlled by chemical equilibrium. The mixture fraction concept and the minimization of the Gibbs free energy are used to compute the result of combustion. Evolution of nitrogenous and sulfurous pollutants is taken into account in a post processing stage (finite-rate reactions for both thermal and fuel-bound NO_x formation and chemical equilibrium for SO_x production). Steady-state operation simulations have been performed to describe the influence of superficial velocity, initial waste composition and power generated by the in-bed boiler on the furnace exhaust, obtaining good qualitative agreement for a 1MW unit.

A steady-state one-dimensional model for the combustion of wood in an atmospheric bubbling fluidized bed reactor is presented by Khan et al. (2007a,b). It makes use of the two-phase theory of fluidization with the assumption of perfect mixing between the solid and the gas in the emulsion phase.

The bed is isothermal at the same temperature of the gas (the bed temperature is a design variable) and differential mass balance equations are formulated for CH₄, CO, CO₂, N₂, NO, NH₃, O₂, H₂ and H₂O. Devolatilization and drying occur instantaneously with a uniform release of volatiles in the emulsion phase. Particle temperature is evaluated by means of a local energy balance. A discretized population balance including fines due to attrition is developed and implemented to calculate the bed inventory and elutriation rate. Char combustion is described according to the shrinking core approximation with a rate constant including a diffusive and a reactive contribution. A sensitivity analysis of the gaseous emission profiles with respect to input and model parameters indicates that gas hydrodynamics play an important role. However, based on model and experiment results, optimization of operating parameters and air-staging ratio can significantly improve the reactor performances.

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