Mathematical Modeling of Entrained Flow Reactors

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Abstract

Aim of this paper is to present and discuss a general model of entrained flow reactors. This device reaches high temperatures and flash heating rate conditions which are very useful to study the devolatilization process of different solid fuels, such biomasses, plastics, coals and solid wastes. A mathematical model is presented focusing the attention both on the description of mass and heat transfer processes at the particle and reactor scales and on the chemical characterization of solid fuel devolatilization and gas phase evolution. Several comparisons with experimental data show the capability of the model in pyrolysis conditions, while these comparisons also indicate the limit of the model to study coal ignition in combustion environments and suggest for possible model modifications and improvements.

1. Introduction

The growing energy demand of developing countries generally finds the answer in fossil fuels. The larger availability and lower cost of coal makes it the leading energy resource for the electric production in the world. On the other hand, coal is a source of environmental concern. For these reasons, clean coal technologies are becoming nowadays attractive and remarkable, aiming at a higher efficiency and a careful emission control. Also thermal conversion of biomasses to produce fuel via gasification is considered as a very promising process because this solid is a CO₂-neutral energy resource. This renewed scientific and technological interest pushes the development of reliable models to support the design and optimization of both furnaces and gasifiers of solid fuels. Experimental data obtained in Entrained Flow Reactors (EFR) are very useful to further develop and validate multistep kinetic models of biomass and coal devolatilization recently presented [2,3].

2. Mathematical model of the EFR

Mathematical models describing the EFR behaviour, such as the core-annular reaction zone, were recently discussed in the literature with special emphasis to the fluid dynamics aspects inside the tube [4]. With the development of Two Fluid Model (TFM), more detailed coal particle processes can be described including particle drag and turbulent dispersion, heat-up, volatilization, drying and heterogeneous combustion.

The numerical model here adopted focuses the attention mainly to the description of mass and heat transfer processes at the particle and reactor scales, and also to the chemistry of solid fuel devolatilization.

Three main sub-models are combined to obtain the global mathematical model of the EFR:

a. the kinetic model of solid fuel (coal, biomass,..) devolatilization;

b. the particle model;

c. the reactor model.

2.1. 2.1 The Kinetic Model of Fuel Devolatilization

Mechanistic models of biomass and coal pyrolysis and gasification are applied at the particle scale with inclusion of the successive reactions of released species in order to account for the
gas-phase kinetics. Beside heat and mass transport processes, a mechanistic model of solid fuel gasification and pyrolysis should focus on three different facets of the overall process:

1. devolatilization of the fuel, i.e. the decomposition of the solid into permanent gases, condensable vapors (tars) and solid residue (char);
2. successive or secondary gas phase reactions of the released gas and tar species;
3. char gasification, i.e. the overall set of heterogeneous reactions of the steam with the solid residue, that is usually much slower of the previous stage.

During the last two decades, structural models have been developed that tend to describe more accurately the chemistry of devolatilization. These models were initially developed for coal and more recently have been applied to biomasses [5,6]. They are more focused on the solid decomposition itself and not on the detail of the released species and their successive gas phase reactions. The multistep kinetic models of devolatilization of biomass [2] and coal [3], recently developed, are here applied to describe both the fuel devolatilization and the successive gas phase reactions. Biomasses are simply described in terms of cellulose, hemicellulose and lignin, while coal is described with three different reference coals (lignite, bituminous and anthracite). Chemistry of the released species in the gas phase are described with their primary propagation and decomposition reactions down to species already included in a general detailed kinetic model of pyrolysis, partial oxidation and combustion. The whole reaction scheme, constituted by hundreds of molecular and radical species involved in several thousands of elementary and lumped reactions, is available online in CHEMKIN format at [www.chem.polimi.it/CRECKModeling/]. Char residue is assumed as pure carbon and usual kinetic laws are then used to describe its oxidation and/or gasification. Two different reference char components are assumed in order to partially characterize the nature of the char as well as the effect of the annealing process.

2.2. The fuel particle model

The fuel particle model is based on mass and energy balances over the particle and gas phase boundary conditions. The complexity of these models strongly depends on the description level of the time evolution of the solid matrix. On the basis of this transformation, the physical properties of the solid and the transport properties of the diffusing gases are derived. The solid fuel particle, which consists of a mixture of reference components and ash, is assumed as a homogeneous sphere with NS internal sectors that account for possible heat and mass transfer resistances. Gases are released by the particle to the surrounding gas phase while surrounding gases diffuse into the solid particle.

The mass balances for the $i^{th}$ species in the $j^{th}$ spherical sector is given by:

$$\frac{dm_{i,j}}{dt} = J_{j-1,j} - J_{j,j} + (1 - \varepsilon_j) V_j M_i \sum_{k=1}^{NR_{part}} \left( \nu_{i,j,k} \cdot r_{j,k} \right)$$

(1)

The contribution to mass flow rate $J_{j,j}$ in the mass balance equation results:

$$J_{j,j} = -\Gamma_{j,j} \frac{dC_{j,i}^{part}}{d\xi} \cdot S_j \cdot \varepsilon_j$$

(2)

The flux exchanged $J_{i}^{DEV}$ with the gas phase at the external surface is:

$$J_{i}^{DEV} = K_i \left( C_{NS,i}^{gas} - C_{i}^{gas} \right) \cdot S_{NS} \cdot \varepsilon_{NS}$$

(3)

The energy balance for the $j^{th}$ spherical sector includes the conduction terms, the enthalpy contributions associated to the mass fluxes and the reactions duties:
where the last term is the total heat production rate due to chemical reactions. The model takes into account both the heat fluxes due to the radiation between particles and reactor wall and the thermal power exchanged with the gas phase; the latter term is calculated at the external surface \((j=\text{NS})\) in the following way:

\[
q = U \left( T_{\text{NS}}^\text{part} - T_{\text{gas}}^\text{gas} \right) \cdot S_{\text{NS}}
\]

Released tar components can either mix with the surrounding gases or, at lower temperatures, can condensate on cold surfaces. Gas phase is considered as a perfectly stirred reactor inside the cell module. Convective fluxes or flow rates entering and exiting the module are allowed, both for gas and solid phase. This elemental module is flexible and suitable for simulating different process alternatives, such as fixed or moving bed gasifiers and combustors, updraft or downdraft configurations and also the entrained flow reactor, as it will be discussed in the next section. The C++ BzzDAE solver is used to numerically handle this mathematical model [7]. Physical and mathematical details on the overall complexity of this problem are given elsewhere [8].

### 2.3. Mathematical Model of the Reactor

Gas and solid particles move with different velocity inside the EFR. The slip velocity, i.e. the relative velocity of gas and solid particle \(v^\text{gas} - v^\text{part}\), needs to be properly evaluated in order to account not only for the contact times inside the reactor, but also for the proper evaluation of heat and mass transfer coefficients. The gas velocity \(v^\text{gas}\) is usually nearly constant along the whole reactor. The particle velocity \(v^\text{part}\) is derived from the momentum balance equation on the single particle, accounting for buoyancy and drag forces. The slip velocity for 0.5 mm particles asymptotically approaches values of \(\sim 0.60\) m/s after \(\sim 0.15\) cm, while the slip velocity for the 1.0 mm particles at the reactor outlet is more than 2 m/s.

The mass balance equation of the \(i^{\text{th}}\) gas phase species inside the EFR is given by:

\[
\frac{dW_i^\text{gas}}{dt_p} = v^\text{part} \cdot A \left( \eta \cdot J_i^\text{DEV} + W_i \sum_{k=1}^{NR_{\text{gas}}} \left( \nu_{i,k}^\text{gas} \cdot \nu_{k}^\text{gas} \right) \right)
\]

where the total concentration of solid particles in the gas phase can be expressed as:

\[
\eta = \frac{\bar{m}}{v^\text{part} \cdot A \cdot m_p}
\]

Energy balance equations of the solid and gas phases are treated with the same assumptions already described for the mass balance equations. The gas enthalpy balance becomes:

\[
W_G \cdot C_p^\text{gas} \frac{dT_{\text{gas}}}{dt_p} = v^\text{part} \cdot A \left[ \sum_{k=1}^{NR_{\text{gas}}} \left( -\Delta H_k^\text{gas} \cdot \nu_{k}^\text{gas} \right) \right] + \eta \left( \sum_{i=1}^{NC} J_i^{\text{DEV}} h_{i,\text{NS}}^\text{part} + q \right)
\]
3. Comparisons with experimental data

As already mentioned, the EFR model is extensively applied to study the devolatilization and combustion of both biomass and coal particles. High temperatures, flash heating rates, residence times of \( \sim 1 \) s are typical conditions of these reactors.

3.1. Pyrolysis experiments: Biomass and Coal

The roasting and charification of .4-1.1 mm biomass particles in an alumina tube of 0.075 m diameter electrically heated was already discussed by Dupont et al. [10]. Maximum temperature of 1250 K and residence times of .2-5 s were considered. Both the composition of released gases and solid residue well compare with experimental measurements. The gasification reactions of char residue are too slow to occur under these pyrolysis conditions.

A second example, already discussed in a previous paper [3], refers to the role of secondary gas phase reactions in the pyrolysis of coal particles in high pressure EFR experiments. The high pressure and the significant residence times increase the role of pyrolysis reactions of tar components. Fletcher and co-workers already observed the difficulty of steady operations in the pressurized drop tube reactor at 900-1100 K, because of relevant soot formation and coke deposit on the reactor wall [11]. Experimental measurements indicate average oxygen content in tar components of \( \sim 5-13\% \) and \( \sim 5-6\% \) of hydrogen. Increases of the pyrolysis temperature led to the increase of carbon content in tar mainly accompanied by the decrease of oxygen content. Similar values of oxygen are also measured in coal chars, while hydrogen content is usually lower than 3\% and it decreases with pyrolysis severity. Secondary gas phase pyrolysis reactions explain these differences. We analysed the reactivity of the released components from Adaro coal in a mixture with 90\% mol He, in typical operating conditions of the pressurized drop tube reactor. Secondary reactions increase with increasing severity and the net effect is to convert tar fraction into gases and heavy components, improving in this way the agreement between predictions and measurements. Dealkylation and decomposition reactions, as well as condensation reactions of aromatics are responsible of this gas production. Aromatic structures gradually move towards heavier polycyclic aromatic hydrocarbons (PAH), like coronene and ovalene, well recognized soot precursors.

3.2. Coal Ignition and Combustion

Two different sets of experimental data are here analysed. The first refers to the ignition behaviour of different rank coals, by varying the oxygen content in the gas flow [12]. The latter data relate to single coal particle combustion at high temperatures in \( \text{O}_2/\text{N}_2 \) and \( \text{O}_2/\text{CO}_2 \) environments [13].

3.2.1. Ignition behavior of different rank coals [12]

The reactivity and ignition behaviour of coal particles is of considerable importance for designing and controlling the combustion process. Coal particles can ignite either homogeneously, where the initial step is the pyrolysis and ignition of the volatiles followed by the ignition of the char, or heterogeneously, which involves the direct attack of oxygen on the whole sample particle. An electrically heated entrained flow reactor (170 cm length with internal diameter of 4 cm) was used for the ignition studies [12]. Coal was entrained in the primary carrier gas at ambient temperature and introduced into the furnace with a preheated secondary gas. Residence time of \( \sim 2 \) s were analyzed with temperatures up to 1350 K. Seven coals of varying rank and different volatile matter content (which of course exerts a strong influence on ignition behaviour), were studied, from high volatile bituminous (PE: Chile) with 50\% volatile matter up to a semi anthracitic coal (HV: Spain) with only 10\% of volatiles and 90\% C on daf basis. Figure 1 shows the ignition behaviour of PE coal particles at reactor temperature of 973 K with the three different secondary gases: Air, 8\% \( \text{O}_2 \) in \( \text{N}_2 \), 4\% \( \text{O}_2 \) in \( \text{N}_2 \).
The ignition is a homogeneous ignition of the released gases, the sudden rising of CO₂ corresponds to CO consumption and, of course, ignition in air is faster than the remaining ones. The maximum of CO₂ is very close to the experimental value, while lower amount of CO are experimentally observed.

Ignition temperature of PE coal at 900-920 K reasonably agrees with experimental observation, while the temperatures of coal particles are not experimentally reported. It is important to note that particle temperatures are still too low to justify a significant heterogeneous combustion of the residual char. This fact is more evident when analysing the ignition behaviour of the semi anthracitic HV coal. Figure 2 shows the temperature of the coal particles at three different initial temperatures: 1023, 1123 and 1223 K. Figure 2a clearly evidences a first homogeneous ignition and only after the successive heterogeneous ignition. Only at coal temperatures of ~1300 K, the char combustion takes place in a significant way and only a minor residual char is present at the reactor outlet. This fact is particularly evident in figure 2b, where residual char is reported versus the reactor length. Ignition temperature of about 1100 K is observed for anthracitic coal, accordingly with experimental data.

3.2.2. Coal particle combustion at high temperatures (1400 K) [13]

This investigation burned pulverized coal in a vertical drop-tube furnace under two different gas mixtures (O₂/N₂ and O₂/CO₂) at varying O₂ partial pressures and very high temperatures. The goal was to obtain temperature–time profiles and to investigate the impact of replacing N₂ with CO₂ on particle combustion behaviour. Figure 3 reports model predictions for the bituminous coal particles (45–180 μm). The temperature of the coal particles reaches values of about 2200 K in the O₂/N₂ system, while lower temperatures are reached when replacing N₂ with CO₂, because of the different heat capacity. All these values well agree with experimental measurements. Figure 3 also shows the predicted and observed char burnout times of the bituminous coal both in O₂/N₂ and in O₂/CO₂. Model predictions are close to the average experimental values, but model cannot distinguish between the two
systems. Temperatures are large enough and, as expected, a mass transfer regime is observed, without apparent influence of the temperature. Note that the effect of CO$_2$ gasification reaction could not contribute to explain this point. This aspect requires a further analysis with a more careful estimation of transport and system properties.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Coal particle burnout [13]}
\end{figure}

4. Conclusions

A simplified approach for simulating gasification and combustion of solid fuels in entrained flow reactor has been developed. The model takes into account the mass and energy transport between the gas and the solid phases, as well as the kinetics both in the solid and gas phases. Despite the several simplifications introduced to reduce the overall cpu time, the models are able to reproduce the main phenomena and especially the trends with the coal range and with the operating conditions. These characteristics make this tool an interesting support at the design and optimization level.

Acknowledgments

The Authors gratefully acknowledge the financial support of CNR-DET in the behalf of the MSE research project ‘Carbone pulito’.

References

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