Review of devolatilisation models and their application to pulverised fuel combustion simulation

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Abstract

This paper reviews biomass devolatilisation models from literature, including single first order reaction as well as parallel reaction models. The performance of these models is evaluated with experimental data obtained in drop tube furnaces, for which detailed information was available on the axial temperature profile. One model of each type led to very large volatile yield in accordance with the experiment using sawdust. The other models led to a more limited volatile release and compare well with experimental data from hazelnut shells that retained part of the tar release as documented in the experiments report. This shows the specificity of the empirical models reviewed. The application of the CPD model adapted for biomass had good results for a heating rate of $10^3 K/s$, but it predicted an early mass loss for higher heating rates with limited volatile yield.

Numerical simulations were carried out for two furnaces, the first 150kW, using natural gas only or mixed with coal or sawdust, while for the second 10 MW, the distribution of the mass sources from particles was analyzed. The results for the natural gas flame show some differences from the experimental data due to the incorrect calculation of recirculation zones. The co-firing with coal and sawdust, show a different behavior that is analyzed numerically changing independently density and diameter. For the larger furnace the behaviour of the particles is also observed to be different with sawdust being more easily entrained without significant penetration in the internal recirculation zone.

Keywords: Numeric Simulation, Devolatilization, Co-Combustion, Biomass.

1. INTRODUCTION

The higher interest on the discovery of alternative energy solutions is pushed, mainly by three reasons. The negative environmental impact, consequence of the massive energy production from fossil fuels and nuclear, increment of associated anxiety around the potential end of the fossil fuels and at last the insecurity of potential accidents on the nuclear energy production.

One of the strategies to solve this natural and society problem, on a short period of time, consists on the use of biomass combustion. This is a process with a neutral balance on the carbon life cycle (an advantage to the reduction of greenhouse effect) and prevents potential fires at forests. The preferential types of biomass fuel are the ones that have themselves a sustainable cultivation (forests) and fiscal privileges associated.

There are two alternative solutions for biomass combustion, either using it in dedicated installations where they require less preparation or using biomass in pulverised form for co-combustion with fossil fuels. In the later case the co-combustion with coal is more feasible since as it is also a solid fuel that has also to be pulverised. In case biomass is already available in powder form (e.g. sawdust) it can also be used with other fossil fuels, e.g. with natural gas.

A numerical model is a tool to support the development and application of co-combustion by analysing the interactions that may occur between the different fuels. Their trajectory depends on the flow and particle properties that are quite different between coal and biomass. The solid fuel particles exposed to hot gases inside the furnace exchange heat by convection and radiation and their mass loss can be represented in three sequential stages – drying, devolatilization (volatile freedom and combustion in a homogenous gaseous phase) and char combustion. The impact of each stage can be estimated from the ultimate analysis of the solid fuel. For biomass the volatiles account for most of the mass as well as the main contribution for heat release.
Following this introduction the paper presents in section 2 the numerical models that were used namely in 2.1 a comparison between the devolatilisation models and their classification while in 2.2 the CFD based numerical model used to simulate the furnaces is briefly described. Section 3 presents the comparison of the devolatilisation models with experimental results selected from well-documented test cases at high heating rates obtained in drop tubes. In 3.2 results of the simulations obtained using the CFD based model are presented and compared with the relevant experimental results or between the situations of coal and biomass. Finally section 4 presents conclusions from the present work.

2. NUMERICAL MODELS

2.1 - Devolatilisation models for biomass

Volatilisation models have been developed since the early seventies including biomass. The modelling approach has been based on experiments and on data interpretation, estimating the role of physical mass and heat transfer to reveal the intrinsic role of kinetics. This approach allows the definition of kinetic data for certain temperature ranges. For wood or other biomass materials some authors suggest [1,2] that the behaviour of these materials depends on their components, that is cellulose, hemi-cellulose and lignin. Biomass also contains less known extractives that are also combustible and can be more easily driven off.

The mass loss in the simpler volatilisation models has been adjusted in Arrhenius form to fit the influence of temperature and in some cases considering a distribution of activation energies to represent the release of different molecular weights of particles. Earlier models were derived based on experiments performed with large samples such as the studies of Roberts and Clough [3], leading to the definition of an activation energy of 69.1 kJ/mol.

The activation energy of the global reaction rate (k) presents widely variable values, roughly comprised between 56 and 174 kJ/mol. This can be the result of the different heating conditions established in the experimental devices, which include tube furnaces, entrained and fluid bed reactors, screen heaters, drop tubes and classical thermo-gravimetric, the different sample characteristics (size or mass and wood/biomass variety) and the mathematical treatment of the experimental data. Indeed there are three specifically ranges separated by the temperature range and test conditions investigated: (1) The high temperature data [4] (up to 1400K) presents typical values of 69-91KJ/mol and the low-temperature data (below 700-800K) where two ranges can be distinguished, (2) experiments where intra-particle heat and mass transfer limitations may be important with 56-106 KJ/mol [1] and (3) experimental data with higher values 125-174 KJ/mol [5].

The volatilisation studies early recognized the presence of different gas species in the volatiles. These have been characterised e.g. in the experiments by Nunn et al. [4]. In general however most authors have only distinguished the release of very different molecules from the particles, namely permanent gases and tars that condense once the products are cooled. The role of the tars is very important since they may suffer thermal cracking producing further light gases or on the other hand may deposit and condense contributing to the formation of char particles.

Based on the different factors mentioned above and on the use of very different type of experiments to characterise the volatilisation process, it is easier to understand that there are different results influenced by the specific characteristics of the experiments and the interpretation of the data. The main apparatus used to obtain volatilisation data are drop tubes, flat flame burners, fluidised beds and wire mesh or other type of systems to hold small samples.

The type of models obtained in the literature can be classified in different categories depending on the level of detail and reactions considered. A classification is given below to identify the models and to present the kinetic data review.

Models that represent only the mass loss of particles are fitted with a single first order volatilisation rate, expressed in Arrhenius form. The rate may be expressed for the volatile mass loss as proportional to the remaining volatiles to be released and in this case the volatile yield is specified. In this case volatile release is expressed as:

Type A

\[
\frac{dY_v}{dt} = -k \times (Y_v^* - Y_v)
\]  

(2.1)
where $Y_v^*$ represents the ultimate yield of volatiles.

Alternatively mass loss is expressed as a function of the biomass mass fraction but in this case there is no indication of the amount of char formed. In this case mass loss is expressed by:

$$\frac{dY_B}{dt} = -k \times Y_B$$  \hspace{1cm} (2.2)$$

Table 1 presents the kinetic parameters (pre-exponential factors and activation energies) for the rate constants for first order devolatilisation models. The table includes the particle sizes, temperature range considered in the experiments, as well as the type of apparatus where the data was obtained.

**Table 1 Kinetic constants for mechanisms of wood/biomass pyrolysis with single reaction.**

<table>
<thead>
<tr>
<th>Author</th>
<th>Feedstock (size, mass)</th>
<th>Experimental system</th>
<th>Rate Type</th>
<th>Temp.Range [K]</th>
<th>$Y_v^*$</th>
<th>$E_a$ [kJ/mol]</th>
<th>$A$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gordon &amp; Knight[4]</td>
<td>Hardwood, 300-350µm</td>
<td>ITF</td>
<td>B</td>
<td>677-822</td>
<td>-</td>
<td>89.5</td>
<td>1.48E8</td>
</tr>
<tr>
<td>Tognoti[6]</td>
<td>Hazelnut shells, 150µm</td>
<td>DTR</td>
<td>B</td>
<td>973-1273</td>
<td>-</td>
<td>49.2</td>
<td>2500</td>
</tr>
<tr>
<td>Nunn et al [4]</td>
<td>Sweet gum hardwood, 45-88µm, 100mg</td>
<td>Screen Heater (1000K/min)</td>
<td>A (symmetric expression)</td>
<td>600-1400</td>
<td>0.93</td>
<td>69.1</td>
<td>13.4E4</td>
</tr>
<tr>
<td>Stamm [4]</td>
<td>Red fir, 1.59<em>25.4</em>149.2mm</td>
<td>FB</td>
<td>A</td>
<td>440-573</td>
<td>0.71</td>
<td>124.8</td>
<td>2.88E7</td>
</tr>
<tr>
<td>Roberts &amp; Clough [3]</td>
<td>beech tree, 10 mm</td>
<td>DTR</td>
<td>A</td>
<td>626-778</td>
<td>0.72</td>
<td>62.8</td>
<td>1.51E3</td>
</tr>
<tr>
<td>Thurner &amp; Mann (single) [1]</td>
<td>Oak Missouri, 615 µm</td>
<td>DTR</td>
<td>A</td>
<td>573-665</td>
<td>0.70</td>
<td>106.3</td>
<td>7.41E5</td>
</tr>
</tbody>
</table>

The mass loss can also be expressed as the sum of three rates representing the formation of the different products that are: light gases, tars and char. This is the parallel reaction model that is represented schematically in figure 1. Figure 1 also includes a secondary step for the conversion of tar into light gas and char. These processes may become occur within the particle for larger sizes, high temperatures and given sufficiently long residence times. Secondary reactions of tar vapors are classified as homogeneous and heterogeneous and include processes such as cracking, partial oxidation, re-polymerization and condensation.

![Fig.1 One-component mechanism of primary wood pyrolysis proposed by Shafizadeh and global mechanism for the secondary reactions tarry species as proposed by Antal [adapted from 9].](image)

The rate of formation of each product is proportional to the unconverted biomass mass fraction and can be expressed by:

$$\frac{dY_i}{dt} = -k_i \times Y_B$$  \hspace{1cm} (2.3)$$

where $i$ refer to the product formed (see Fig.1).

Table 2 presents the kinetic parameters for parallel reaction models. The last model indicated considers also the secondary reactions based on a previous model for the primary decomposition.
and sizes of aromatic rings elements, interlinking by a different chemical bridges: "labile bridges" and "charred bridges" (attached during the thermal degradation).

Further to the empirical models mentioned above, the CPD (Chemical Percolation Devolatilisation) model [10] was also considered. This model is based on a molecular structure with different types and sizes of aromatic rings elements, interlinking by a different chemical bridges; "labile bridges" (easily break during the pyrolysis) and "charred bridges" (attached during the thermal degradation).

Table 2 Kinetic constants for mechanisms of wood/biomass pyrolysis with single reaction.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Thurner and Mann [1]</td>
<td>Quercus Rubra, 650 µm</td>
<td>ITF</td>
<td>573-673</td>
<td>G</td>
<td>106.5</td>
<td>7.4E3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T</td>
<td>112.7</td>
<td>4.12E8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>88.6</td>
<td>1.43E4</td>
</tr>
<tr>
<td>Wagennar [5]</td>
<td>Pine 100-125 µm</td>
<td>TGA</td>
<td>553-673K</td>
<td>G</td>
<td>125</td>
<td>3.05E7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DTR</td>
<td>773-873K</td>
<td>T</td>
<td>149</td>
<td>9.28E9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>177</td>
<td>1.11E11</td>
</tr>
<tr>
<td>Font [8]</td>
<td>Almond Shells, 300-500 µm, 2mg</td>
<td>Pyroprobe</td>
<td>733-878K</td>
<td>G</td>
<td>139.2</td>
<td>1.52E7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T</td>
<td>119</td>
<td>5.85E8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>73.1</td>
<td>2.98E8</td>
</tr>
<tr>
<td>Hong Lu [9]</td>
<td>Sawdust 320 µm</td>
<td>Pyroprobe</td>
<td>733-878K</td>
<td>G$_r$ *</td>
<td>107.5</td>
<td>4.28E3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DTR</td>
<td>573-708K</td>
<td>C$_r$ *</td>
<td>107.5</td>
<td>1.00E3</td>
</tr>
</tbody>
</table>

* These refer to the secondary reactions from tar forming gas (G$_r$) and char (C$_r$). The Hong Lu model is based on the primary reaction kinetic parameters of Font model.

Summing the rates of product formation in the parallel reaction model leads to the rate of biomass decomposition and taking the fraction of light gas and tar allows the definition of volatile mass loss. This was calculated to compare the rates from the parallel reaction models with the single first order reaction models. The rate of biomass decomposition obtained from the sum of the parallel reaction models has only an Arrhenius form if the activation energy of all reactions were the same. From table 2 it can be observed that the difference between gas and tar activation energies is lower than 10%.

Figure 2 presents a comparison of the kinetic rates for both single and parallel reaction models indicating the temperature ranges considered by the different authors. There is a large range of values for the kinetic parameters to the biomass’s mass loss, partly explained by the testing procedures. In general it can be observed that the values are lower for higher temperature.

![Fig.2 Arrhenius plot for the global decomposition rate of wood/biomass based on one-component mechanisms.](image-url)
The CPD model was adapted for biomass [2], specifying structural parameters for the biomass components (cellulose, hemi-cellulose and lignin) and adjusting the kinetic parameters for the different processes from low heating rates test results. A correlation was proposed for the components content as a function of the ultimate analysis of biomass and the model was favourably tested with the results from Nunn et al [4] with an estimated heating rate of 1000 K/s.

The devolatilisation models tested were compared with one-dimensional biomass pyrolysis experimental results [6, 9, 4]. Five devolatilisation models were compared in the present work. One first single order reaction [4], three models with parallel-competitive reactions [1, 5, 9], one of them with secondary reactions [9] and the CPD model [2]. For all the models the cumulative particle mass loss was calculated along the trajectory, assuming a uniform consumption within the particle.

2.2 – CFD based numerical model

The numerical simulations were performed using the FURNACE code [11] and PF2 code. The latter is a simplified version of the first, in which one-dimensional calculations are made for the particles solving the motion equation, energy and mass balance to the particle, based on a Lagrangian calculation. This is the approach used in the CFD based model [11] for multi-dimensional problems, where balance equations are applied to the gaseous phase in an Eulerian base.

The gaseous phase has a type of flow field calculated through axial, radial and tangential momentum balance equations. The pressure distribution is calculated from the continuity equation using the SIMPLE algorithm. A turbulent viscosity is used based on a two-equation $k-\varepsilon$ model. The combustion reactions take place on a gaseous phase (defined by $O_2$, CO, CO$_2$, H$_2$O, CH$_4$ and tar mass fractions).

Three main reactions are considered the first two for methane (R1) and tar (R2) oxidation and in both CO is assumed as a product. Then the oxidation of CO (R3) is also considered as this is an important intermediate specie and it arises also from char combustion.

$$\text{CH}_4 + 3/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} \quad \text{R1}$$

$$\text{C}_x\text{H}_y\text{O}_z + (x-z)/2 \text{O}_2 \rightarrow x \text{CO} + y/2 \text{H}_2 \quad \text{R2}$$

$$\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2 \quad \text{R3}$$

The rates for these reactions are based in a combination of kinetic rates from the literature and a turbulent mixing rate estimated from the EBU (Eddy Break-Up) model. The mixing time in this model is calculated from the eddy life time (proportional to $\varepsilon/k$) [11].

The energy balance to the continuum gaseous phase has two energy sources as a consequence of: (1) interaction with the particles, including heating, drying and char combustion and; (2) radiative heat transfer calculated with the discrete ordinates method using radiation gaseous properties from the SLW model [12].

Trajectories are calculated for representative particles applying Newton law with drag and gravity forces. At the same time particle temperature is calculated from an energy balance and based on the calculated temperature the mass loss is evaluated considering in sequence the particle evolution (drying, devolatilization and char combustion). The selected particles are chosen at random positions in the correspondent inlet and with diameters according to a specified distribution discretized in about 10 values.

The application of the model was done in a radial plane using cylindrical coordinates assuming axisymmetric. This is the conditions for the IST furnace [13] where the grid was implemented with 94 and 75 control volumes respectively in the axial and radial directions. The calculations for mass sources for the IFRF furnace [12] that was a square cross section furnace were performed in an equivalent radial plane with a grid of 102x110.

3. NUMERICAL RESULTS

3.1 Comparison of devolatilisation models

Data from literature was examined and two data sets [6, 9] with small particle sizes under conditions of pulverised fuel were used to compare the models. Fig. 3 presents a comparison of the mass loss along time calculated by all the models reviewed compared with the measured mass loss of Hong Lu using sawdust [9]. This data was obtained for high temperature (1350 K) and shows that only two of the models represent the actual volatile yield; while all the others lead to a more limited value. The
single reaction model of Nunn et al [4] besides giving the correct level of volatile yield presents a better fit with the experimental data. It should be noted that the results from Hong is based on another parallel reaction model obtained previously [8] and was not fitted to his own data [9].

All the other models led to a lower value of volatile yield although the volatilization rates are all comparable. The CPD model adapted to biomass [2] was found to give a very early volatile release compared with the empirical models. This model was set with low heating rate data and tested with the data of Nunn et al [4] for 1000K/s but does not produce acceptable results for the larger heating rates that occur in the high temperature drop tube.

Further comparisons were done with the mass loss history of hazelnut shells based on data from Tognotti et al [6] but in this case the biomass conversion is limited due to the capture of some of the volatiles within the particles. The experiments are conducted with air so there is some char combustion but this has a minor contribution to the mass loss according to the calculations along time. The comparison of mass loss as a function of nominal reactor temperature is presented in Fig. 4, where it can be observed that the models identified above [4, 9] overpredict the mass loss while the other models provide a good agreement with the measured results. In this case according to the observations made by Tognotti et al [6] there are internal mass transfer limitations insulating some of the volatiles released within the particle. Tests were performed to evaluate the influence of particle diameter that was small within the range used in the experiments.

Further tests were performed to compare the models performance against the lower heating rate data of Nunn et al [4]. The CPD model leads to good results as it was tested for these results. All the other models lead to a delayed mass release but provide a reasonable estimate in all cases of the char fraction. Figure 5 presents the comparison of the tar yield as a function of temperature for the parallel reaction models and CPD. From this figure it can be observed that from the parallel reaction models, the model of Hong [9] provides a better prediction of this product.
Based on the tests considered the models from Nunn et al [4] and Hong [9] were selected for application in CFD based numerical modeling. The first one estimates the mass loss and does not identify the tar fraction so the volatiles are considered with an average composition. Using the parallel reaction model causes problems to the application of the model once there is the need to specify the gas composition and to define the tar composition. This was solved using average values of the gas composition as characterized by Nunn et al [4].

3.2 CFD based numerical simulations

Figure 6 presents the calculated flow patterns, represented by stream functions for the IST furnace test cases, corresponding to 1) Natural gas flame and co-combustion with 2) coal and 3) sawdust. This figure includes the mass release from the coal and sawdust resulting from the calculations. The results of the simulations showed that including coal and then biomass reduced the extension of the internal recirculation zone as presented in Fig. 6. The consequence for the particles is that in case 3 the deflection of the main flow from the burner is smaller and therefore the particles are further entrained releasing volatiles and burning in a more concentrated pattern. The mass release from coal is more uniform and includes a larger contribution within the internal recirculation zone.
Fig. 6 Comparison of flow patterns and mass release in the cases of 1) natural gas, 2) NG with coal and 3) NG with biomass. These cases are based on the test conditions of Casaca [13].

Fig. 7 presents a comparison between the calculated and measured temperature profiles.
From figure 7 it can be recognized that there are important deviations mainly in the second profile. The first profile shows that the secondary air flow has a larger radial expansion that is connected with the calculation of the internal recirculation zone (IRZ) closer to the burner than suggested from the experimental data. As a result, most of the combustion is predicted to occur between the internal and external recirculation zones, leading to a temperature peak in the second profile, while the experimental data suggests that at that profile the main jet flow was not yet deflected and hence the larger temperature observed. These effects have consequence for the later profiles.

Taking the limitations into consideration, it is still worthwhile pointing out that the predicted influence of coal and wood close to the burner is in agreement with the measured data, showing to a reduction in temperature that is larger for the coal particles. From the mass source distribution in fig. 6 it can be observed that sawdust is mostly entrained between the recirculations and mass sources are more concentrated in the external part of the furnace close to the wall.

The behavior of co-firing coal and biomass was analysed based on the numerical results of Rocheta [12] for the IFRF case C using flue gas recirculation and oxygen injection. Figure 8 presents a comparison of the mass release patterns from coal and from biomass. This calculation was done based on the converged solution of coal combustion.

The results from figure allow the observation that for the same gas flow field the coal particles have a stronger penetration in the internal recirculation zone while the biomass particles (sawdust) with larger diameter and smaller density are more easily dragged by the flow and therefore do not have a significant penetration in the internal recirculation zone. These results are in line with the previous ones showing that the biomass particles owing to their smaller inertia may not mix so easily as in the case of coal particles. This has some important implications for the ignition, since the different particle flow leads to the release of volatiles not in the main area where coal should be ignited. This implies also that the conclusions taken from the ignition behavior obtained in reactors with almost uniform flow may not have a direct application in the case of the co-firing coal-biomass flames.

Fig. 8 Flow patterns and mass release for RFG+O2 flame from IFRF tests for cases of coal and biomass using two different models [1, 5].
4. CONCLUSIONS

Devolatilisation models were reviewed and their performance compared for test conditions relevant to pulverised coal combustion with high heating rates [6, 9]. Two of the models [4, 9] led to the volatile yield shown in the experimental test using sawdust, while all the others, including the CPD model led to a lower value. The lower value however is representative of the results obtained for hazelnut shells where some tar may have been captured within the particle [6]. The comparisons made for the tar yield suggest also that the model of Hong [9] is the only to predict the correct level of this product.

The CFD based numerical simulations of IST furnace show significant differences with experimental data that can be partly explained by the location and dimensions of the recirculation zones. The influence of coal and biomass co-combustion with natural gas is correctly indicated by the model. The mass sources from biomass and coal particles are significantly different as a result of their different trajectories in the furnace. This shows the importance of using CFD based models to interpret co-combustion of biomass and coal.

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